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selenide which would be formed during the heating at the expense of the wires.

Exp. 3.—For the purpose of testing this conjecture, a number of cells were constructed of Se having incorporated with it cuprous selenide in different proportions. The wire used was platinum; it was of the same gauge in all cases (0.27 millim.), and the number of turns per unit of length was also the same (10 per centim.). The surface area, however, varied somewhat, and in order to facilitate comparison the figures, as given in the annexed table, express in each case the resistance of a square centim. of surface. The light employed was always, except where otherwise stated, that derived from an 8 candle-power incandescent lamp, the filament of which was 1 ft. (about 30 centim.) distant from the face of the cell. None of the cells containing added selenide were annealed, but were cooled as soon as the Se had crystallized. That in which there was no Cu_2Se was annealed for six hours. For comparison, the table is headed with particulars of a good ordinary copper-wire cell of similar dimensions.

TABLE I.

Composition of Cell.	Annealed or Unannealed.	Percentage of added Cu_2Se .	Resistance in dark of 1 sq. cm. Megohms.	Percentage decrease in light.
Cu Wire and Se	Well annealed	0	0.7	45 to 50
Pt Wire and Se	„ „	0	13.9	33
Pt wire and Se + Cu_2Se	Unannealed.	0.5	12.0	32
„ „	„	1.5	14.7	57
„ „	„	3	3.6	47
„ „	„	4	0.90	38
„ „	„	5	0.25	28

In the cell containing 1.5 per cent. of Cu_2Se , the thickness of the Se coating was accidentally made much less than the diameter of the wires, instead of equal to it, as in the other cells: hence its unduly high apparent resistance and its

correspondingly great sensitiveness (for its exposed surface was disproportionately great). In other cases the results are as regular as could be expected. They demonstrate clearly enough that a cell of fairly good sensitiveness and conductivity may be formed without any annealing, if a suitable quantity of metallic selenide be first added to the Se. They also render very evident the fact that an excessive quantity of selenide, while it reduces the resistance to a comparatively low point, only does so at the cost of the sensitiveness. This agrees with the well-known fact that an ordinary Se cell whose resistance has been unduly lowered by too long heating is only moderately sensitive to light. Exactly what part is played by the free selenium remains yet to be determined; it is certain that cuprous selenide by itself is quite insensible.

§ 6. *Sensitizing Insensitive Selenium.*

During the last fifteen years I have worked with a great many different samples of Se, and have observed that they did not all possess exactly the same degree of sensitiveness: some were better than others, but the sensitiveness of the best was probably not more than 8 or 10 per cent. greater than that of the worst. Lately, however, I have been supplied commercially with a batch of selenium which, under the usual treatment, is almost absolutely insensitive to light. This Se differs a little in appearance from the ordinary article. In the vitreous condition its colour is of a lighter shade, and its surface is less lustrous than usual. When melted (above 217°) it forms a tenacious semi-fluid mass, which adheres like treacle to the mica and spatula and is difficult to spread; it does not exhibit the capillary effects previously referred to, and at a suitable temperature it crystallizes with great rapidity. It has not been analysed, but such impurities as it may contain probably do not include the metallic selenides commonly met with*.

Exp. 4.—Three copper-wire cells of the usual size were made with this Se and annealed for several hours. Their resistances in the dark had the abnormally high values of 170,000, 290,000, and 520,000 ohms respectively, the last

* Two other samples of insensitive Se have since been supplied to me from different sources.—*June 28th.*

named being very thinly coated. When illuminated by the incandescent lamp at 12 inches, the decrease of the resistance amounted in the case of the first two to only a fraction of 1 per cent. (instead of the customary 40 or 50 per cent.), and in the thinly-coated cell to about 6 per cent.

Exp. 5.—Two perfectly similar copper-wire cells of smaller size were coated, one with the insensitive Se and the other with ordinary Se, and annealed side by side for $5\frac{1}{2}$ hours. On subsequently testing, the resistance of the ordinary cell was found to be 20,500 ohms in the dark and 40 per cent. less when illuminated, while that of the other was 780,000 in the dark and only 2.5 per cent. less under illumination.

Exp. 6.—A cell was constructed having exactly the same dimensions as those last mentioned, and was coated with insensitive Se with which 3 per cent. of cuprous selenide had been previously incorporated. It was not annealed, but cooled gradually during about fifteen minutes. Next day its resistance in the dark was 190,000 ohms, and when illuminated by the lamp, 140,000, the decrease being 26 per cent.; in sunlight it fell to 43,000 ohms, or 77 per cent. less than in darkness.

Exp. 7.—Another cell of the same size was made in which 5 per cent. of selenide was added to the insensitive Se. Its resistance in the dark was 105,000 ohms, and when illuminated by the lamp 79,000, a fall of 25 per cent.

Exp. 8.—Another similarly sized cell had 3 per cent. of lead selenide mixed with the Se. Its resistance dark was 363,000 ohms, and illuminated $10\frac{1}{2}$ per cent. less.

It appears, therefore, that the addition of a small quantity of cuprous selenide imparts a fair degree of sensitiveness to the anomalous Se, at the same time bringing down its resistance to nearly the normal value. An equal proportion of lead selenide produces a similar, though less marked effect. It would be interesting to try selenides of arsenic and other metals, but I have not yet had time to do so.

It is certain that an ordinary well "annealed" Se cell with copper electrodes contains a relatively large quantity of copper selenide. Mr. W. Hibbert was kind enough to analyse the Se taken from one of my old cells to which no foreign substance had been intentionally added, and found that it

contained 2.28 per cent. of combined copper, equivalent to 3.71 per cent. of cuprous selenide. Of course this must have been derived mainly from the copper electrodes.

§ 7. *Effect of Time.*

The fact that the resistance of crystalline Se with metallic electrodes fused into it decreases very greatly in course of time was first noticed by Prof. W. G. Adams and Mr. R. E. Day*, who thought that it was due to the Se having become more completely annealed. In a former paper† I have suggested that the decrease is more probably to be attributed to the short-circuiting of the cell by an excessive amount of conducting selenide, formed by the gradual union of the Se with the metal of the electrodes. This view receives strong support from the following observations.

Exp. 9.—In the year 1891 I constructed a copper-wire cell but did not crystallize nor anneal the Se, which remained therefore in the vitreous state: its resistance was sensibly infinite. The cell was laid aside in a box until March 1895, when it was tested and its resistance found to have fallen to about 8 ohms. The cell was quite unchanged in appearance, the selenium surface being perfectly black and glossy. The decrease of resistance could not possibly be accounted for by spontaneous crystallization, and could hardly have been due to any other cause than the formation of selenide in the interior. The cell was unfortunately destroyed before it occurred to me to use it for an experiment like the following.

Exp. 10.—A cell made in 1881 had then a resistance of about 100,000 ohms and was very sensitive to light. In 1895 its resistance had fallen to 10 ohms and it was quite insensitive. This was connected with a storage-battery of 26 cells, a detector-galvanometer being included in the circuit. When the current was turned on, the galvanometer-needle underwent a momentary strong deflexion and immediately returned to zero. The dark resistance of the cell was then found to have risen to 60,000 ohms, and it was once more sensitive to light. Clearly a short circuit caused by the selenide had been burnt out.

* Phil. Trans. vol. clxvii. pt. i. p. 348.

† Phil. Mag. March 1891, p. 250.

§ 8. *Action of Light in promoting the Formation of Selenides.*

Several attempts to ascertain whether the union of Se with a metal was assisted by illumination resulted indecisively. The following simple experiments are however, I think, fairly conclusive.

Exp. 11.—One side of a thick plate of copper was evenly coated with red amorphous Se by causing the fumes of boiling Se to play upon it. Half the plate was then covered and the other half exposed, first to diffused daylight and afterwards to sunlight. In diffused daylight the exposed half was perceptibly darkened in the course of two or three hours; in sunlight it quickly assumed a dark chocolate colour, the screened portion remaining bright red.

Exp. 12.—Two pieces of mica were similarly treated, but the exposed portions were not perceptibly darkened by prolonged exposure to sunlight. They became, however, covered with a slight "bloom," like that seen on a ripe plum, which I am inclined to attribute to the formation of an oxide.

Exp. 13.—A brass plate coated with red Se was exposed to sunlight in a photographic printing-frame under a design cut out of black paper and intended to represent a butterfly. A perfectly sharp and intense print of the design was produced upon the red Se. This was made on April 17 last: it has since been kept in the dark and is now exhibited to the Society.

The chocolate colour is closely matched by that of a mixture of red precipitated Se and cuprous selenide in about equal parts.

§ 9. *The Effect of Temperature upon the Resistance of Crystalline Selenium.*

Text-books and dictionaries of chemistry appear to be about equally divided upon the question whether the resistance of crystalline Se is increased or diminished by rise of temperature. There are high authorities for both opinions. In a paper published in 1883* I gave an account of some expe-

* Phil. Mag. Jan. 1883, p. 31.

riments which indicated that the resistance of Se, "or rather perhaps of selenium cells," as I was careful to add, became a maximum at a certain temperature, which varied a little with different specimens but was generally a few degrees higher than the average temperature of the air. Eight different cells were tested, showing well-defined maxima at temperatures of 13° , 14° , 22° , 23° , 23° , 24° , 25° , and 30° respectively.

On further investigating the subject I have traced this curious effect to the action of the fused-in electrodes. So far as I know from a great number of experiments, a piece of crystalline Se into which wires have been fused *always* acquires a maximum resistance at a certain temperature. On the other hand, the resistance of a piece having external electrodes pressed into contact with it is *always* diminished by a rise of temperature.

Exp. 14.—A rectangular plate of Se was cast in one of the white-glazed earthenware "pans" in which moist water-colours are sold. Two platinum wires were made red-hot, and their ends embedded along the shorter sides of the rectangular plate a little below the surface. The plate was then crystallized and annealed and its surfaces smoothed with glass-paper.

The plate was suspended inside an air-bath, the bulb of a thermometer being in contact with it, and the resistance between the platinum-wire electrodes was taken at temperatures ranging from -2° to 12° . The results, which are given in the second column of Table II., indicate that the resistance was greatest when the temperature was 6° .

The same plate was then placed between two pads of india-rubber covered with tinfoil which served as electrodes, and were pressed into good contact by a weight of 500 grammes. The arrangement was placed in the air-bath, and the resistance between the opposite faces of the plate observed at various temperatures. As is shown in the third column of Table II., the resistance diminished steadily as the temperature rose.

TABLE II.

Temperature. Degrees C.	Resistance between Electrodes fused into ends. Megohms.	Resistance between Electrodes pressed against surface. Megohms.
-2	45.6	
0	48.7	
2	52.0	38.5
4	52.3	36.8
6	53.3*	34.0
8	52.5	30.2
10	49.6	26.6
12	46.7	23.9

* Maximum.

Thus with rising temperature the resistance of the *same* piece of Se appears to reach a maximum when measured between fused-in wires, and to decrease *ab initio* when measured between electrodes which are pressed upon its surface.

Beyond doubt the resistance of the Se really falls in both cases. The apparent preliminary rise when the electrodes are fused in, is due to the unequal heat expansion of the Se and of the metal. The coefficient of linear expansion of Se is twice as great as that of copper and three times as great as that of platinum. The effect of heating is to loosen the tight grip of the Se upon the metal and so to increase the resistance of the junction. The rate at which this junction-resistance increases is at first greater than that at which the specific resistance of the Se diminishes: soon, however, the latter effect predominates, and thus the resistance of the combination of Se and a metal passes a maximum.

§ 10. Porosity of Crystalline Selenium.

The consideration of certain phenomena, which will be referred to later, led me to believe that crystalline Se, not-

withstanding its metallic appearance, must be a sensibly porous substance. Experiments were made with the view of ascertaining whether this was the fact.

Exp. 15.—One end of a brass tube was closed by a polished disk of crystalline selenium, 11.2 millim. in diameter and 1.25 millim. thick, which was tightly fixed by an indiarubber collar: to the other end was attached a glass tube which terminated in an open point about 3 millim. in diameter. The whole of the indiarubber and the edges of the Se disk were thickly coated with shellac varnish. The closed end of the tube was dipped into water and air was forced into the open end. No bubbles were formed upon the Se: if therefore Se be porous its pores must be very small.

Exp. 16.—A transpiration experiment was then made. The tube was fixed in an upright position with the Se disk at the top and the glass point at the bottom, the latter dipping into a basin of water. A wide-mouthed glass bottle was supported mouth downwards over the tube, enclosing its upper end. Coal-gas was slowly admitted into the bottle from a small nozzle. The indiarubber tube conveying the gas was for seven feet (about 2 metres) of its length coiled up in a vessel of cold water. When the gas was first admitted water rose for a short distance inside the glass tube owing to the cooling effect of the refrigerated gas: but after a minute or two it began to descend again, and soon air-bubbles were slowly but regularly given off at the pointed end. This continued until the bottle of gas was removed, when the bubbles at once ceased and the water again began to rise in the tube.

Crystalline Se is therefore sensibly porous, and no doubt absorbs moisture from the air.

§ 11. *The Polarization of Selenium by Currents.*

Among the many remarkable properties of Se which were first observed by Prof. W. G. Adams and Mr. R. E. Day in their well-known research, is the power it possesses of setting up a secondary or polarization current after being disconnected from a battery. As all who have worked much with Se must know, the opposing and ever varying electromotive force of polarization renders it very troublesome to make accurate resistance tests by the ordinary bridge method. Unless it is

worth while to expend a considerable amount of time, one has to be contented with two or at most three significant figures, and even this degree of accuracy cannot be attained unless care is taken to depress the battery and galvanometer keys only for a moment*.

In a former communication I stated my belief that these polarization effects resulted from the electrolysis of the metallic selenides contained as impurities in the Se. Whether this be so or not, the following experiments plainly indicate that the presence of moisture is necessary for the production of the phenomenon.

Exp. 17.—The electrodes of a Se cell were connected first with the poles of a battery, and then by means of a “change-over” switch with a galvanometer: this produced a deflexion of 90 divisions, indicating an E.M.F. of rather more than $\frac{1}{100}$ volt. The cell was then placed in a glass receiver over strong sulphuric acid, the connecting wires being passed through an indiarubber stopper. From time to time it was successively joined to the battery and the galvanometer, and the polarization current was observed to be gradually diminishing. After 18 hours the deflexion was only 3 divisions. The air was then exhausted from the receiver, and 24 hours later no polarization current whatever could be detected, even after prolonged connexion with the battery. A current greater than $\frac{1}{300}$ part of that which occurred in ordinary air would certainly not have escaped observation.

Exp. 18.—The cell was afterwards suspended for an hour in a receiver over a basin of water and then tested for polarization. The spot of light was immediately deflected far beyond the limits of the scale.

Probably therefore the polarization results merely from the electrolysis of water; in any case the presence of water seems to be requisite for its production.

It is perhaps worth noting that little if any polarization is exhibited by crystalline Se of the coarsely granular form obtained by gradually *lowering* the temperature of the molten

* If the battery key be kept down for a few seconds, and after it is raised the galvanometer key be depressed, a considerable deflexion due to the secondary current will generally be observed. For exact measurements it is necessary to balance to a constantly changing false zero.

substance, instead of by heating solid vitreous Se. The specific resistance of this form is much lower than that of the other, and its sensitiveness is also less.

§ 12. *The Effect of Moisture upon Conductivity and Sensitiveness.*

The water ordinarily present in Se, even if it had no other effect, would naturally influence its apparent conductivity by acting as a shunt or alternative path for the passage of the current. We should expect, therefore, that if a cell were made as dry as possible, its resistance would be increased, and this was found to be the case.

Exp. 19.—A cell with a Se surface measuring 4 centim. by 1.5 centim., and containing 64 turns of 0.19 millim. copper wire, was suspended in a receiver over sulphuric acid, and tests were made of its resistance both in darkness and under illumination by an 8 candle-power lamp at 30 centim. The results are given in Table III.

TABLE III.
Selenium Cell in Receiver over H_2SO_4 .

Time. Hours.	Resistance. Dark.	Resistance. Illuminated.	Percentage Decrease.
0	50,400	25,400	49.5
28	83,000	35,500	57.2

The dark resistance of the cell, it will be seen, increased in 28 hours from 50,400 to 83,000 ohms : if, therefore, the water which it originally contained acted like a metallic shunt, its resistance taken alone must have been about 128,000 ohms. Now it was found that a thin plate of Se, after having been dried over sulphuric acid for 22 hours, lost $\frac{1}{2800}$ part of its weight. The weight of the Se in the cell used in the present experiment was about 0.4 gramme ; probably, therefore, it originally contained about $\frac{1}{7000}$ gramme of water. Knowing the dimensions of the cell (which are given above), it is easily calculated that if this quantity of water when uniformly dis-

tributed between the electrodes of the cell offered a resistance of 128,000 ohms, its specific resistance must have been approximately 7800 ohms. This is of the same order of magnitude as the specific resistance of good distilled water, though that of purer water is of course much higher. We may fairly conclude, then, that absorbed moisture plays no active part in diminishing the dark resistance of Se, but behaves merely as if it were an inert shunt.

As regards *sensitiveness*, moisture might conceivably exert one of four different influences. If it acted simply as a shunt, its removal ought to increase the sensitiveness of the cell in an easily calculable degree. If its presence were essential to the chemical or physical change which is effected by the agency of light, then a perfectly dry cell would also be perfectly insensitive. If moisture, without being indispensable, were yet in some degree favourable to the operation of light, the sensitiveness of the cell, though it might possibly be increased when the water was withdrawn, would still not be so great as if a metallic shunt of equal resistance had been cut out. Lastly, if the influence of water were positively prejudicial, its removal would result in a greater increase of sensitiveness than if it had been a mere shunt.

The figures in Table III. seem to show that the presence of water, though not essential to sensitiveness, does to some extent assist the action of light. The percentage decrease of the resistance of the dried Se under illumination is considerably greater than that of the undried, but still it is not so great as it would have been if a shunt of 128,000 ohms (the resistance of the water alone) had been withdrawn. In the latter case the resistance of the dry cell in the light would have been only 31,700 ohms instead of 35,000, and the percentage decrease 61·8 instead of 57·2.

Exp. 20.—Three cells were at different times constructed, and after being kept for some hours at a temperature of about 200° were without any previous cooling transferred as rapidly as possible to the sulphuric acid receiver. All turned out to be sensitive to light while in the dry air. Unless, therefore, Se can condense moisture in its pores at a temperature of 200°, which is not probable, its sensitiveness to light is not

entirely dependent upon the presence of water. Having regard to the observations detailed in the next section this was contrary to my expectation.

§ 13. *Attempted Electrolysis of Metallic Selenide.*

Many abortive attempts were made to ascertain whether cuprous selenide conducts electricity entirely like a metal, as is generally believed, or like an electrolyte, as required by my hypothesis. The experiments of which an account is given in this section appear to show that if the conduction is not altogether electrolytic, it is under certain conditions, at least partly so. It must, however, be admitted that the results, though of considerable interest, cannot be regarded as conclusive. The condition requisite for apparent electrolysis is that the surface of the selenide should be moist, a condition of course suggestive of some secondary action.

Exp. 21.—A mass of cuprous selenide about 2 millim. in thickness was placed between two platinum foil electrodes, each of which was covered with four layers of filter-paper moistened with distilled water. The arrangement was pressed together by a weight of 28 lbs. (12·7 kilos), ordinary precautions being taken to avoid short-circuiting. A current averaging 0·03 ampere was passed through the moist selenide for about four hours. On examining the papers afterwards, it was found that those which had been in immediate contact with the selenide were stained a dark grey colour, due evidently only to transferred particles of selenide. The other papers had received stains which differed greatly in appearance according as they were upon the anode or the kathode.

On the *anode* papers the stains were scarlet, and I satisfied myself that they were beyond doubt due to red amorphous Se. For (1) stains of a precisely similar hue and character were obtained by electrolysis a solution of selenious oxide contained in a pad of filter-paper, though of course in this case the stain appeared upon the kathode. (2) The stains turned dark brown when heated. (3) They were not affected by cold hydrochloric acid, as red oxide of copper would have been. (4) Nor by sulphuric acid. (5) Nor (unless very slowly) by cold nitric acid. (6) Hot nitric acid quickly dissipated them. (7) So also did a mixture of cold nitric and

hydrochloric acids. (8) The red stuff could be volatilized at a temperature below that at which the paper was scorched.

On the *kathode* papers the stains were of a dark brown, nearly black, shade, surrounded by small irregular patches of green, blue, and orange. The dark-brown stuff acquired a metallic copper-coloured lustre when burnished, which is sufficient proof that it consisted, largely at all events, of finely divided metallic copper. It was ascertained that if a little of the selenide itself were finely powdered, rubbed into moist paper and dried, no such metallic appearance was produced by burnishing.

The experiment was repeated several times with variations in the details: *e. g.* in one case the selenide was fused with an excess of Se, in another with an excess of Cu. But it was invariably found that red stains were formed at the anode, and almost invariably traces of metallic copper appeared at the *kathode*.

This experiment naturally led me to try to obtain electrically liberated selenium in larger and measurable quantities.

Exp. 22.—Some selenide of copper was prepared by heating together 126 parts of shredded copper-foil and 79 of crushed Se in a closed crucible to bright redness. The product was an iron-grey, cindery-looking mass.

A fragment of this was held in a brass clip, and the lower portion of it dipped into a beaker of water opposite a strip of Pt foil. The selenide was joined to the negative pole of the battery, the Pt to the positive: thus the water was made the anode in relation to the selenide. A current of 0.025 ampere was passed for half an hour. In a few minutes after starting, the water had become scarlet and quite opaque with suspended red Se. Unfortunately, however, the selenide was very friable, and numerous small particles were detached from its surface by the hydrogen bubbles which formed upon it; these became mixed with the liberated Se and made it impossible to ascertain the weight of the latter.

Exp. 23.—In order to obtain a more coherent substance, two parts of Se were thoroughly incorporated with one of Cu_2Se ; the mixture was then fused in an earthenware mould, and thus formed into a rectangular plate weighing 1.0731 gramme. Se itself being a very bad conductor, it was believed

that practically the whole conduction would take place through the selenide. The plate was immersed in water with a strip of Pt, and a current averaging 0.023 ampere was passed for ten minutes. As soon as the circuit was closed the black plate began to give off dense red clouds; and when it was dried and weighed after the experiment, it was found to have lost 0.0250 gramme. If the decomposition had been primarily electrolytic, the weight of liberated Se, assuming its electrochemical equivalent to be 0.00082 *, would have been no more than about half that amount, namely 0.0113 gramme. The red Se was filtered out of the water and examined for particles of *débris*. None were detected by the unassisted eye, but under the microscope many became visible, though whether in sufficient quantity to account for the observed excess of weight is somewhat doubtful.

Exp. 24.—This was a repetition of the last, except that the plate contained six parts of Se to one of Cu_2Se (instead of two to one) and weighed 1.0223 gramme. The current, which averaged 0.016 ampere, was left on for 30 minutes. The actual loss of weight was 0.0386 gramme; the calculated loss, according to the electrolytic law, being 0.0236 gramme. In this case, therefore, with a weaker current and a less friable mixture, the observed exceeded the calculated loss by only 64 per cent. instead of 121 per cent. as in the previous instance. The microscope again revealed the presence of numerous small black particles. The closer approximation is in favour of the possibility that the excess might have been due to the disruption of fragments of the selenide. Further experiments, which need not be detailed, leave the point still doubtful.

This effect of electrical action may be exhibited in a striking manner as follows:—A sheet of moistened filter-paper is laid upon a metallic plate, preferably of Pt, which is in connexion with the positive terminal of a 50-volt battery; a pencil formed of one part of Cu_2Se and six parts of Se is connected by a flexible wire to the negative terminal. When this black pencil is drawn over the paper, it makes a bright red mark

* The electrochemical equivalent of hydrogen multiplied by the atomic weight of Se $= 0.000010384 \times 79 = 0.000820336$. Quite possibly, however, the E.C.E. of Se is only half this value.

which is immediately broken off if the current is interrupted or reversed. If a copper plate be used, the marks will be brown instead of red.

The red stuff separated in the foregoing experiments turned black when heated, and fused and crystallized like ordinary Se. The resistance of a small cell made from a portion of it was 65 per cent. lower than the average; the cell was very sensitive to light, the diminution of its resistance under illumination being 53 per cent.

The question naturally presented itself, whether the separation of the red Se might not in some not easily imagined manner be due to the hydrogen liberated from the water, and not primarily to the current.

Exp. 25.—To test this a zinc wire 1.7 millim. in diameter was coated with a fused mixture of Se and Cu_2Se and immersed in dilute sulphuric acid. The acid penetrated the pores of the coating, and soon small bubbles of hydrogen began to rise from the surface, continuing for about 5 hours. The coating was then broken up, and it was found that all the zinc inside it had been dissolved. A microscopic examination of the fragments failed to disclose the smallest trace of any red Se.

The experiment was repeated with the substitution of ordinary commercial Se, and the same negative result was arrived at. It was ascertained that sulphuric acid did not dissolve the red stuff.

Exp. 26.—An experiment was arranged with the view of determining whether the current exerted any action, real or apparent, upon Se itself when unmixed with any metallic selenide except such as it might contain as an accidental impurity.

A well-annealed plate of crystalline Se having a Pt electrode fused into one edge was supported in water, the electrode being about 5 millim. above the surface. A slip of Pt foil was also immersed, and the two were joined respectively to the terminals of a storage-battery of 26 cells. Until the current had been passing for more than 24 hours, there was no perceptible discoloration of the water. Shortly afterwards it was found that the plate was surrounded by a slight red deposit just above the water-line, and that the lower part of

the water had become pink. On examination, it appeared that the red stuff proceeded entirely from a small hole in the plate above the water-line : the Se was therefore broken up and the course of the hole, which was full of water, was traced and found to terminate very near the Pt electrode, where no doubt platinous selenide existed.

This experiment, though not conclusive, tends to show that Se unmixed with selenide is not acted upon by the current. It is possible that moist crystalline Se may be converted into the red amorphous form by electrical action, but the question cannot be definitely settled until perfectly pure Se is obtainable.

§ 14. *Photoelectric Currents.*

Another of the interesting discoveries of Adams and Day was the fact that an electromotive force could be set up, and a current started in annealed Se merely by the action of light*. This observation has been fully confirmed by subsequent experimenters, and the belief has been expressed that the phenomenon affords an example of the direct conversion of the energy of light into that of electricity. Others have held the opinion that the effect is of a purely thermoelectric nature. My own investigations have led me to the following conclusions :—

(1) The effect is undoubtedly due to light and not to heat ; or, more accurately, it is brought about by the action of radiation, and not by change of temperature.

(2) The energy of the photo-electric current is primarily of chemical or voltaic origin, and is not derived from radiation. Light merely has the effect of facilitating the chemical process, and can have no further influence when the supply of unused material is exhausted.

Exp. 27.—A rectangular plate of Se measuring $14 \times 11 \times 2$ millim. had Pt wire electrodes fused into its two ends and was “annealed” for several hours. The electrodes being connected with a galvanometer, a piece of magnesium ribbon was burnt near the Se : a deflexion immediately occurred showing a current which ceased as soon as the light was extinguished. By screening the two ends alternately, it was

* *L. c.* p. 333.

ascertained that the effect was produced only at one junction, the other being quite insensitive. (It may happen in different cases that both junctions are sensitive or neither. As will be shown later, sensitiveness points to imperfect electrical contact between the Se and Pt due perhaps to a film of red Se.) The direction of the current through the sensitive end was from Se to Pt.

The Se plate was afterwards placed under a glass receiver with a basin of water, and connected with the galvanometer by wires passing through a caoutchouc stopper. In a minute or so a small current was indicated which, after slowly increasing for about 15 minutes, became constant. While magnesium was being burnt near the receiver, the strength of the current was greatly intensified; even diffused daylight temporarily increased the deflexion to the extent of 150 scale-divisions. The direction of the current was as before from Se to Pt.

The plate was then enclosed in a receiver over sulphuric acid. In 8 minutes the permanent current had completely disappeared, and exposure to diffused daylight caused a deflexion of only 2 divisions. In 20 minutes burning magnesium at a distance of 6 inches failed to produce any effect whatever. The Se had completely lost its power of generating a current under the influence of light.

The natural inference seems to be that Se (or Se containing selenide) is slowly oxidized by water, and that the oxidation is increased by the action of light*. Some points bearing on the question will be further considered in the next section.

§ 15. *The Thermoelectric Quality of Annealed Selenium.*

Adams and Day believed they had obtained evidence that the thermo-electric quality of crystalline Se was altered by prolonged annealing. To use the old-fashioned terminology,

* Later experiments render this doubtful. With Se which does not contain any considerable admixture of Pt_2Se (and perhaps it should be added, which has not been previously used as an anode) the photo-electromotive force appears to be always in the *opposite* direction—from Pt to Se. And this seems to be the case not only with water as the electrolyte, but also with the other badly conducting liquids, such as cænanthol, used by Prof. Minchin.—*June 28th.*

they thought that by the process of annealing Se was raised from its place at the bottom of the thermo-electric series, which the experiments of Matthiessen had assigned to it, to a position somewhere above that of platinum. In other words, if a Se-Pt junction were heated to a temperature slightly above that of the other junctions in the circuit (the latter being at the ordinary temperature of the air), then, if the Se were crystallized but not thoroughly annealed, there would be a current from Pt to Se through the heated junction, but if the Se were well annealed the thermo-current would be in the reverse direction—from Se to Pt.

They applied heat at a junction by directing upon it a blast of hot air from a glass tube terminating in a fine nozzle, the tube being heated over one or more Bunsen burners. Where it was possible, heat was also applied by holding the junction of Pt and Se between the finger and thumb. All the pieces of Se with which they worked had had Pt wires fused into their ends before being annealed.

The following experiments point to a conclusion different from that of Adams and Day.

Exp. 28.—Experiments were made with three different specimens of Se, all of which had been annealed for many hours. None of these had electrodes fused into them. The arrangements were varied in details, and the Pt-Se junctions heated in different ways. In all cases the direction of the thermo-electromotive force was from Pt to Se across the hot junction. The direction of the current was not affected by the addition of platinous selenide to the Se.

Further experiments were made with the Se plate referred to in the preceding section which had Pt wires fused into its ends.

Exp. 29.—The Pt wires being connected with the galvanometer, it was found that when one junction was touched with the finger there was as usual a current from Pt to Se, but that when the other was touched (that which had generated the photo-electric currents in a former experiment) there followed a current in the opposite direction—from Se to Pt.

All the following observations were made with this anomalous junction.

Exp. 30.—The junction was heated by touching it first with the pointed tip of a warmed glass rod and afterwards with a hot copper wire. In both cases there resulted a current in the *normal* direction—Pt to Se.

Exp. 31.—A bent glass tube having a fine nozzle at one end was heated over a Bunsen flame, and air was blown through it from the mouth upon the junction. Result, an *abnormal* current—Se to Pt.

Exp. 32.—The last experiment was repeated, but the air was driven through the tube by a foot-blower. Result, *normal*—Pt to Se.

Exp. 33.—The tube was allowed to cool, and when quite cold air from the lungs was again blown through it. Result, a current from Se to Pt stronger than that obtained with the hot blast in *Exp. 31*.

Exp. 34.—A small piece of sponge moistened with tepid water was held upon the end of a wire near the junction but not touching it. There immediately followed a small current from Se to Pt.

In short, the anomalous current from Se to Pt was in every case clearly started, not by heat but by moisture.

The succeeding experiments indicate that at the anomalous junction the electrical contact between the Pt and Se was imperfect, and that the Se contained a certain amount of platinous selenide.

Exp. 35.—One part of platinous selenide having been incorporated with six parts of Se, the mixture was fused and crystallized. Thus was obtained a button of crystalline Se containing about 15 per cent. of platinous selenide. The button and a piece of Pt foil were partly immersed in water and their dry ends connected to the galvanometer. A voltaic current was indicated from the button to Pt through the water.

Exp. 36.—The button was dried and tested for a thermo-current with Pt. Result, current from Pt to button through the junction. The button, therefore, behaved thermo-electrically like ordinary Se.

Exp. 37.—By means of an adjustable spring a strip of Pt foil was arranged so as to press lightly on the button. The two were connected with the galvanometer.

Touching the button near the junction with a hot wire caused a current from Pt to button.

Holding the tip of the finger very near the junction without actual contact caused a current from button to Pt.

Blowing air upon the junction from a hot glass tube produced a current from Pt to button when the air-blast was derived from a foot-blower, and from button to Pt when air from the lungs was blown through the hot tube.

Thus all the thermo-effects of the "anomalous" junction were completely imitated. Perhaps in the case of that junction good contact was prevented by a film of non-conducting red Se, or possibly the wire electrode may have been simply loose.

These effects could not be produced when using a button which consisted of Se annealed without contact with a metal and containing no added selenide, the voltaic effect being then similar in direction to the heat-effect.

Summary.

1. The conductivity of crystalline Se appears to depend principally upon the impurities which it contains in the form of metallic selenides. It is suggested that the selenides conduct electrolytically, and that the influence of light in increasing the conductivity is to be attributed to its property of facilitating the combination of selenium with metals in contact with it.

2. The specific resistance of crystalline Se has no definite value but is always very high, varying in the specimens tested from about 30 to 1600 megohms. It is not in general diminished by prolonged heating unless the Se is in contact with a metal (Exps. 1, 2).

3. A Se cell having Pt electrodes and made with Se to which about 3 per cent. of cuprous selenide has been added, is, even though unannealed, greatly superior both in conductivity and sensitiveness to a similar cell made with ordinary Se and annealed for several hours. It is not, however, quite equal to a cell prepared in the usual way with copper electrodes (Exp. 3).

4. A particular sample of commercial Se which, when treated in the ordinary manner, was almost absolutely insen-

sitive to light, was rendered sensitive by the addition of a little metallic selenide (Exps. 4-8).

5. The great fall of resistance exhibited by pieces of Se with fused-in electrodes after the lapse of a few years, is not due to any material lowering of the specific resistance of the Se, but to short-circuiting by selenide formed at the expense of the electrodes. The resistance of an old cell was instantly raised from 10 ohms to 60,000 by connecting it with a 52-volt battery and thus burning out the short circuit (Exps. 9, 10).

6. Red Se in contact with copper or brass is quickly darkened by the action of light, owing, it is suggested, to the formation of selenide. Photographs may be printed on copper or brass coated with red Se and preserved in darkness for a long time (Exps. 11-13).

7. The resistance of crystalline Se always decreases with rise of temperature. The apparent increase of resistance on heating generally observed when the electrodes are fused into the substance, is to be explained by the fact that the heat-expansion of the Se is much greater than that of the metallic electrodes; imperfect contact is consequently produced at the junction (Exp. 14).

8. Crystalline selenium is porous and absorbs moisture from the air (Exps. 15, 16).

9. The polarization of Se after being traversed by a current is due to absorbed moisture (Exps. 17, 18).

10. The moisture ordinarily present in Se renders the apparent resistance much lower than the true resistance of the substance (Exp. 19).

11. The presence of moisture is not essential to sensitiveness, but appears to be in a slight degree favourable to it (Exps. 19, 20).

12. When a current is passed through cuprous selenide between platinum electrodes which are covered with moistened paper, red Se is deposited on the anode paper and metallic copper on the kathode paper (Exp. 21).

13. If cuprous selenide is made the kathode and a strip of Pt the anode in water, red Se mixed with detached particles of the selenide is deposited in the water (Exp. 22).

14. With a mixture of cuprous selenide and Se the quantity of detached black particles is greatly diminished, but the weight

of the separated red Se appears to be greater than that required by the law of electrolytic decomposition. Possibly the current has the effect of converting pure crystalline Se when moistened into the red amorphous variety (Exps. 23, 24).

15. The hydrogen produced by the action of zinc upon dilute sulphuric acid has no effect upon the cuprous selenide nor upon Se in contact with the zinc (Exps. 25, 26).

16. The photo-electric currents sometimes set up when light falls upon Se are dependent upon the presence of moisture and are no doubt of voltaic or chemical origin. (Exp. 27).

17. Experiments which have seemed to place well-annealed selenium above platinum in the thermo-electric series were vitiated by the presence of moisture. Dry Se is always below Pt (Exps. 28-37).

DISCUSSION.

Prof. MINCHIN suggested that the selenium "cell" should be called a selenium "resistance." A grid having one terminal made of aluminium and the other of copper might form a true cell, and might generate an E.M.F. when light fell on it. He would like to know if the author had tried any such cell in which light, simply and solely, generated an E.M.F. He could not agree that chemical action must necessarily follow the action of light in a cell. For take the case of the oldest photo-electric cell—the thermopile,—what chemical action can we show here for all the energy of the incident heat? Chemical action due to light may or may not occur, according to the nature of the cell.

Mr. APPLEYARD asked whether the author had submitted these selenium resistances to the action of electric oscillations. Prof. Minchin's "impulsion" cells were greatly influenced by electric oscillations. The great variation in the resistance with time of the author's cells pointed rather to an effect of contact between the selenium and the electrodes than to an elementary change in the structure or composition. He (Mr. Appleyard) had recently tried to crystallise a super-saturated solution of sodium sulphate by electric oscillations; as well as by direct sparks, and by currents of several ampères; but no crystals could be induced to form. Change of contact

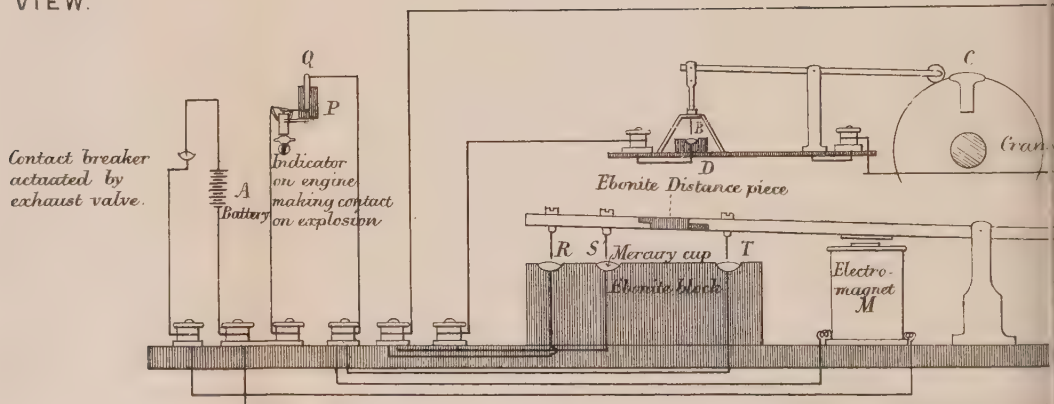
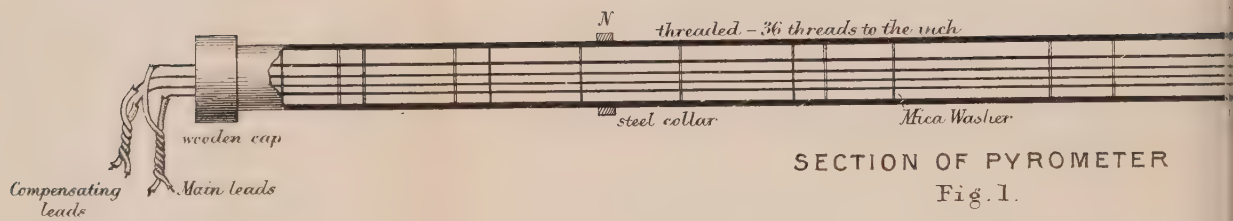
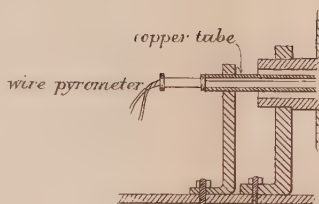


DIAGRAM SHOWING CONNECTIONS FOR CLOSING GALVANOMETER
Fig. 3.



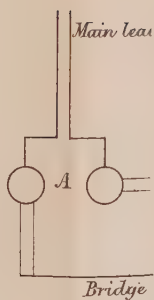
SECTION OF TUBE

the middle of the bridge

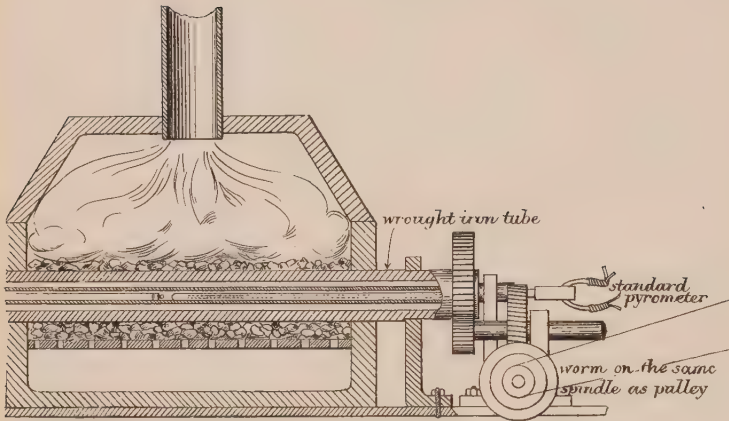
of engine

to the bridge slider through the galvanometer

CIRCUIT.

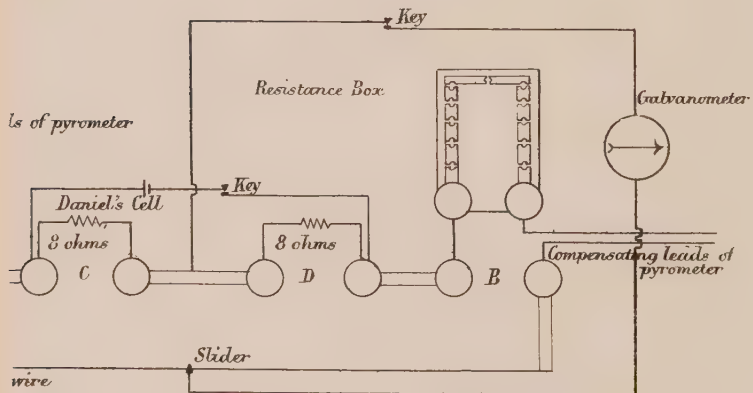


DIAG



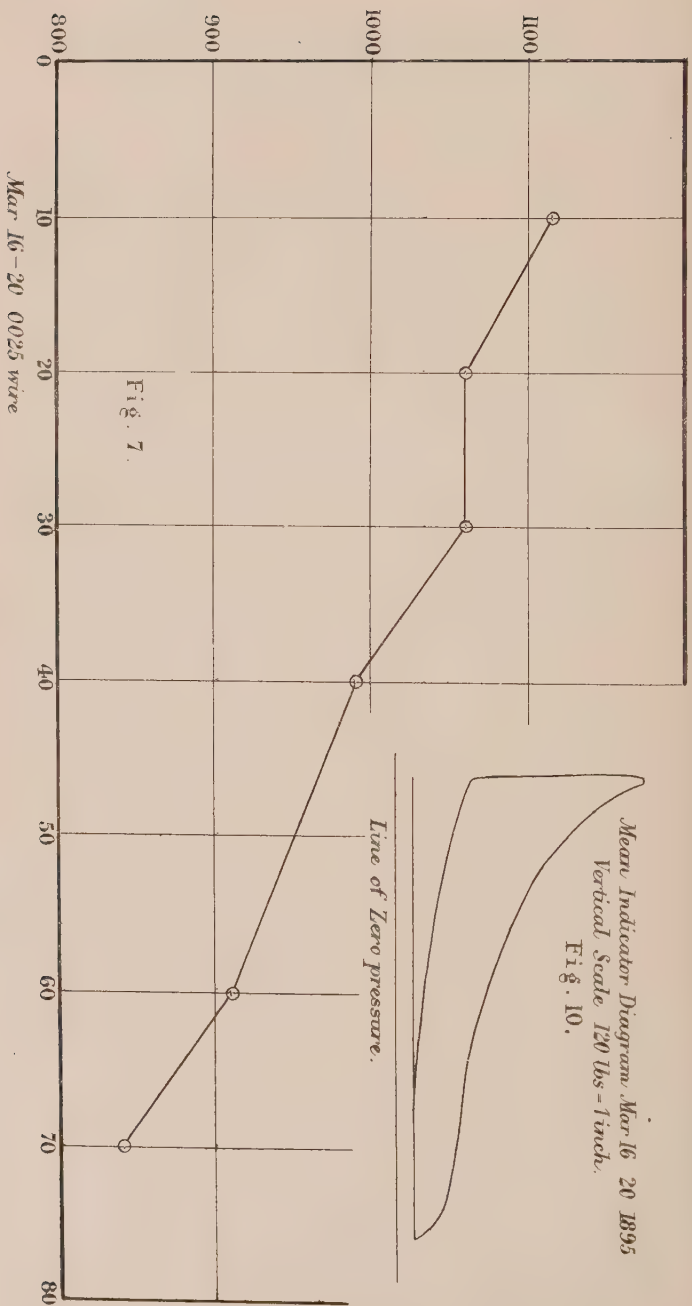
FURNACE SHOWING PYROMETERS IN POSITION.

Fig. 4.



WIRING OF BRIDGE CONNECTIONS.

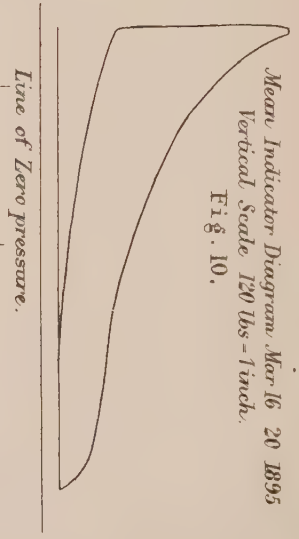
Fig. 2.



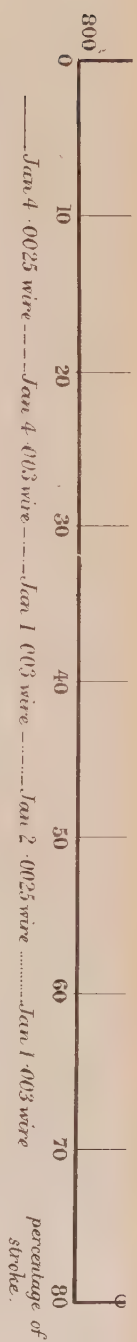
Mar 16-20 0025 wire

Fig. 7.

Minerva Bros lith.



Mean Indicator Diagram, Mar 16-20 1895
Vertical Scale 120 lbs - 1 inch.
Fig. 10.



Mean Indicator Diagram Jan 31 Mar 7, 1895.
Vertical Scale 120 lbs = 1 inch.

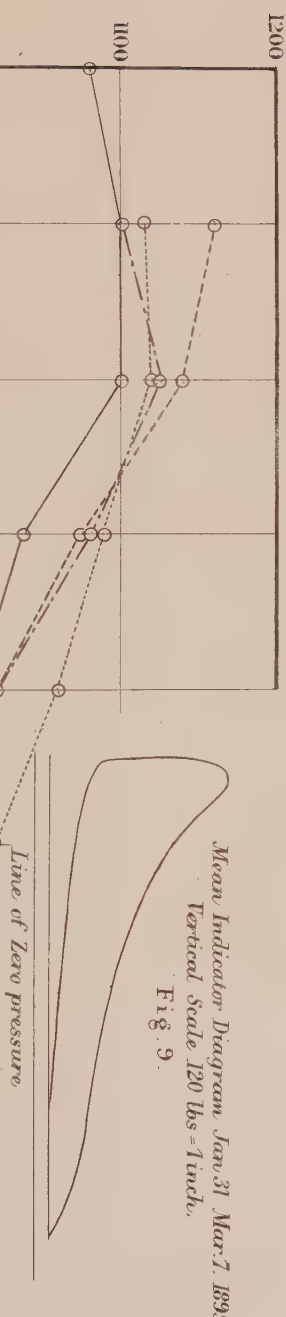


Fig. 6.

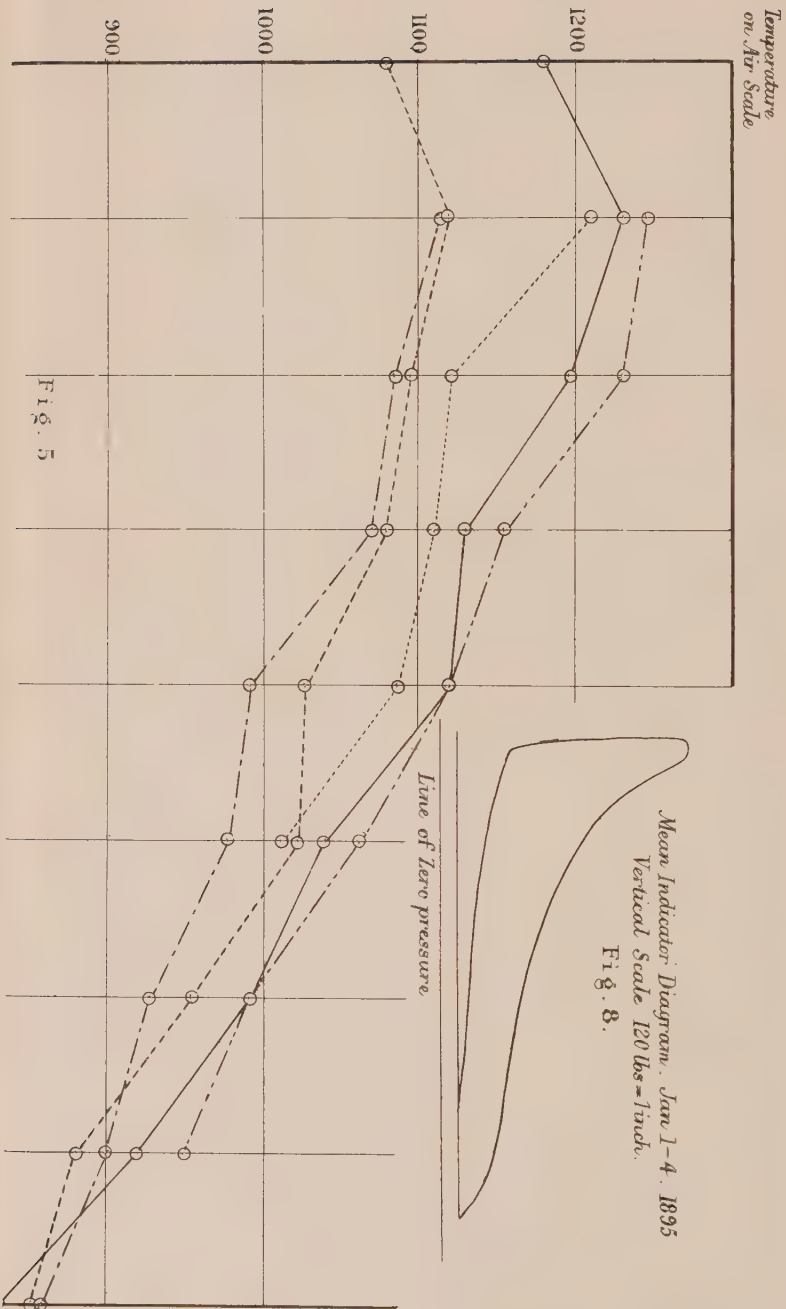


Fig. 5

rather than change of structure appeared to him to be the most promising direction in which to look for an adequate theory of selenium resistances.

Prof. RAMSAY said the quantity of the Se liberated in the electrolytic experiment was much too great to be accounted for by oxygen dissolved in the water. The study of selenium was very interesting, for this substance was on the borderland between those bodies in which the electric conduction was metallic and those in which it was known to be electrolytic.

The AUTHOR, in his reply, said he agreed that the name "selenium cell" was not an appropriate one. He had not tried the effect of electric oscillations.

XLIX. *The Measurement of Cyclically Varying Temperature.*

By HENRY F. W. BURSTALL, M.A., A.M.I.C.E.*

[Plates X. & XI.]

I HAVE been engaged since the latter end of 1892 in attempting the measurement of the temperatures reached in the cylinder of a gas-engine, and the following paper embodies the results which I have obtained.

So far as I am aware no experiments on this subject have been previously published; such attempts as have been made have failed from the want of a sufficiently sensitive thermometer. The platinum resistance-thermometer has, however, proved to have the required sensitiveness, and I shall devote this paper to the description of one of its forms which I have found suitable for the measurement of cyclically varying temperature.

The direct determination of the temperature in the cylinder clears the field for more complete discussion of the theory of the gas-engine, but as I would rather treat the experiments which I have already made as preliminary only, I will not enter into any discussion on this point in the present paper.

I had hoped during this work to have had the collaboration

* Read May 24 and June 14, 1895.

of Prof. Kapper, but unfortunately, owing to the pressure of other work, he was unable to devote the necessary time to these researches. I wish to take this opportunity of thanking him for putting at my disposal the experimental gas-engine at King's College, and also for many valuable suggestions he has made during the course of the work.

The engine used is an Otto cycle-engine. This cycle, which is that now most generally used in internal combustion-engines, is completed in four strokes of the piston.

During the first stroke a charge of mixed air and combustible gas is drawn into the cylinder by the forward motion of the piston, the air- and gas-valves are now closed automatically, and the piston, on its second stroke, compresses the mixture, nearly adiabatically *, into the clearance space. This space forms a prolongation of the working cylinder, and has a capacity of about 45 per cent. of the volume swept through by the piston. The pressure reached at the end of the compression stroke is thus about four atmospheres. At the commencement of the third stroke communication is opened to the ignition-tube; the mixture then explodes, and the pressure rises to about fifteen atmospheres. The piston moves forward and the pressure falls, as the heated gases expand, until it is about three and a half atmospheres. This takes place just before the end of the stroke, and at this point the exhaust-valve opens. During the fourth stroke the products are discharged from the cylinder.

In order to measure the extremely high temperatures which were known certainly to be reached during such a cycle, some special form of thermometer had to be employed: not only is the temperature high, but the pressures to be dealt with are such as to destroy any thermometer not constructed of materials capable of resisting great mechanical stresses. It appeared to me that the platinum resistance-thermometer, which has been brought to such perfection by Callendar and Griffiths, and whose constants can be determined with such a high degree of accuracy, gave the greatest promise of success.

The general form and construction of such thermometers

* During compression the pressure and volume are approximately connected by the relation $pv^{1.3} = \text{constant}$.

are now so well known, that I will only describe the special form which I have employed to fulfil the following conditions, which had to be satisfied in this particular case :—

- (i.) The thermal capacity must be small, as the variations of temperature are extremely rapid. A whole stroke of this engine is completed in less than one fourth of a second; during this time the temperature varies about 500°C. , and as the temperature has to be measured at any fraction of the stroke, a lag of 0.01 second corresponds to one tenth of the stroke of the piston.
- (ii.) The body of the thermometer must be made of some strong material such as iron or steel, as the impulsive pressures would immediately destroy any weaker material.
- (iii.) From the nature of the thermometer chosen, the leads must be well insulated from each other and from the body of the instrument, the insulating material being such as to stand high temperatures.

To fulfil all these conditions was by no means easy. In order to satisfy the first I was forced to employ a naked wire of small diameter, which obviously gives the minimum thermal capacity per unit of surface. I was fully aware that the whole of Callendar and Griffiths's work had been done on wires which were carefully shielded from the least contamination by means of an outer envelope; hence it might have been expected that a naked wire would prove unreliable, but I show later that, provided suitable precautions are taken, naked wires give satisfactory results, at any rate to the order of accuracy of my experiments.

The difficulties of obtaining the requisite mechanical strength, and at the same time good insulation, were very great; and nearly twelve months' work was expended before a satisfactory solution of the problem was obtained. The greater number of the earlier instruments were deficient in mechanical strength. In most laboratory experiments this is seldom of great importance; but this weakness invariably led to the thermometer being blown out of the engine after a few explosions, and the results were disastrous to the experiments.

Description of the Thermometer. (Plate X. fig. 1.)

The body of the thermometer consists of a seamless steel tube 15 inches long and $\frac{3}{4}$ inch outside diameter; the outside of the tube is screwed from end to end with a fine thread. Working on this thread is a nut N, so arranged that the thermometer-wire can be immersed to any required depth in the gas-engine cylinder. For a distance of about one inch from one end, A, the tube is threaded in the interior and a small ring screwed in. Against this ring, which forms an internal collar, rests a circular slate block (C) pierced with four small holes through which the four leads pass. These leads are of platinum, 0.03 inch diameter and 4 inches long. About 1.5 inches from the end A small platinum collars are gold-soldered on to the leads; these prevent the leads from being blown out of the tube, by bearing against the slate block. In the stem of the thermometer the leads are of stout copper soldered with brass to the platinum leads and separated from each other by mica washers. After the leads have been put in position, a packing of alternate layers of asbestos and mica washers is placed on the slate block, as shown in the figure, and by means of the screw-gland D is forced into all the interstices—the instrument thus being made tight under the pressure. Four leads are used, two being joined by the measuring-wire, the other two being joined directly together*.

Description of the Resistance-Measuring Apparatus.

In order to readily eliminate the changes of resistance of the leads, an equal-arm slide-bridge was employed. The connexions are shown diagrammatically in fig. 2.

In the arm A are placed the main leads; in the opposite arm B are the compensating leads in series with the resistance-box. In the arms C and D are two carefully adjusted equal coils, each having a resistance of about 8 ohms. The bridge-wire is of platinum-iridium, and is half a metre long; its resistance is 0.2980 ohm at 15° C. This wire was calibrated by Carey Foster's method, and, for the degree of accuracy

* For permission to use the compensators (the invention of Mr. Calendar), I am indebted to the Cambridge Scientific Instrument Company.

required (0.001 ohm), was found to be of sensibly equal resistance per unit length throughout.

The galvanometer, a very dead-beat astatic instrument, had a resistance of about 100 ohms. The magnet system and mirror were suspended by a quartz fibre 1.5 inches long, and was damped by a specially large mica damper very closely enclosed.

The scale was placed 4 feet from the mirror, so that a change of resistance of 0.0005 ohm could be readily detected.

The resistance-box was an ordinary plug series box with platinoid coils. It was, in the first instance, calibrated by Mr. E. Wilson, of King's College; but after considerable use so much trouble was given and, indeed, so many experiments spoiled through the inefficiency of the plugs, that links, screwed up by a screwdriver, were substituted for them. Although the links are not so convenient to work with as the plugs, the results have been in every way satisfactory since this change. I then re-calibrated the box, and the two determinations were in fair agreement. Below I give a table of the values of the coils used during the experiments:—

Nominal value of coil.	Calibrated value at 11° C.	} In terms of my coil, C.L.C. 417.
ohms.	ohms.	
0.5	0.5063	
1	1.0042	
2	2.0020	
2	2.004	}
5	5.013	

As the working stroke in the Otto cycle only occurs once in four strokes of the piston, and as the temperature had to be measured at particular parts of that stroke, it was necessary that the galvanometer should only be in circuit at the right moment, otherwise the galvanometer swing would not give an indication of the true temperature of the wire. During each explosion stroke the measuring-wire goes through the whole cycle of temperature and, in order to secure a particular epoch of this stroke, the following arrangement of contact makers (shown in fig. 3) was designed. The galvanometer circuit was broken in two places, one of which was made during every working stroke, and the other at a definite

epoch at every revolution; thus the galvanometer circuit was only completely made at one definite point in every working stroke. At any required point in the stroke of the piston, contact is made every revolution by a cam (C) on the crank-shaft of the engine lifting one end of a vibrating lever, depressing a wire (B), fixed to the other end, into a mercury cup D, and thus making a galvanometer contact for a definite time (about $\frac{1}{20}$ of the stroke) at a certain fraction of the stroke. This, however, makes contact once every revolution, while the temperature is measured only during an explosion stroke. To ensure that the galvanometer circuit shall only be made during every working stroke, it is again broken and only made at the proper time by a relay. This relay is on a separate circuit which is completed by means of a steam-engine indicator (P), whose pencil is replaced by a metal point. During the compression and exhaust strokes the pencil bears on a boxwood cylinder, but when the explosion occurs the arm is forced upwards by the pressure and the pointer makes contact on a strip of brass Q, thus completing the relay circuit. The electromagnet is excited and the beam depressed, completing the galvanometer circuit through the mercury cups R and S. As soon as the relay has moved through a small distance, the indicator break is short-circuited by the mercury cup T, and thus the relay circuit remains closed until broken by a contact on the exhaust-valve of the engine. Although somewhat complicated this relay was found to work well, but great care had to be taken that the contacts were all well amalgamated and the mercury clean, otherwise the very small currents in the galvanometer circuit, when a balance is nearly obtained, are entirely broken by any dirt or grease.

To make a determination of the temperature at any required point the contact-maker on the engine-shaft was set, by means of marks on the driving pulley, to make contact at the required position of the piston. An approximate balance was then found by putting a suitable resistance in the box and adjusting the position of the slider on the wire. If the temperature had been the same at the same point in the stroke in every working stroke, an accurate balance could have been obtained by shifting the slider till the deflexion of the

galvanometer was reduced to zero, but this, however, was not the case, and no attempt in the later work was made to obtain an accurate balance on the bridge-wire. The slider was set in such a position that the galvanometer threw about six scale-divisions to one side of zero, and ten successive throws observed. The slider was then moved until the galvanometer threw about six divisions on the other side, and ten throws observed. By taking the mean of these and interpolating, the true reading on the bridge-wire was obtained.

The gas-pressure was rising towards the end of the experiment from 1.6 to 1.9 inches of water.

Below I give a specimen page of my note-book :—

Resistance in box 2.2 ohms.

Bridge-wire.

Galvanometer-throws at	500	200	300
	6 left	3 right	2 right
	5	14	0
	7	5	10
	8	16	3
	7	7	7
	3	15	12
	4	24	5
	10	10	16
	4	15	17
	6	25	3
Mean	6.0 left	13.4 right	7.5 right $\frac{1}{2}$

Taking the throws at 500 and 300 we obtain, by interpolation from the throws, a bridge-wire reading of 407, and taking those at 500 and 300 we obtain a reading of 411.

One division on the galvanometer-scale corresponds to from 15 to 50 divisions of the bridge-wire scale, the former figure being for points towards the end of the stroke, and the latter for points towards the commencement of the stroke of the engine. As a check on this method, I have taken the bridge-wire reading from three points or more instead of two, and have found the results obtained agreed within a few scale-divisions of the bridge-wire. To be accurate, this method presupposes constancy in the testing battery, and in the earlier work considerable trouble was found from the variation of the battery, which was two Leclanché cells. In the later work, both in the determination of the fixed points

of the thermometers and for the experiments in the gas-engine, a single Daniell cell with an added resistance of about 20 ohms was used, and even after many hours' work was found perfectly constant.

There now remains the question, when the resistance of the measuring-wire at any point has been determined, what temperature on the air-scale corresponds to the resistance found. Callendar has shown that if temperature, in degrees Centigrade, be denoted by t , and pt denotes what is called the platinum temperature, then

$$t-pt = \delta \left(\frac{t^2}{100^2} - \frac{t}{100} \right),$$

where δ is a constant which has to be determined for any particular platinum wire; pt is defined as equal to

$$100 \frac{R-R_0}{R_1-R_0},$$

where R_0 is the resistance of the wire in melting ice, R_1 is the resistance of the wire in steam at atmospheric pressure, and R the resistance of the wire at the temperature t^* .

As my thermometers consisted of very fine naked wires which were, of necessity, exposed to the erosive action of high-temperature gases, it could not be expected that the fixed points, *i. e.* the resistance in ice and steam, would remain constant after the wire had been in the cylinder for any length of time. Also, owing to the irregular working of the gas- and air-valves, the temperatures reached in the cylinder sometimes far exceeded the mean. When one of these abnormal explosions occurred the wire was sometimes completely fused, and more frequently melted on the surface. These two causes necessitated a frequent determination of the fixed points and also of the value of δ .

Three sizes of measuring-wire were used: they were all about $\frac{3}{4}$ inch long, their diameters being 0.003, 0.0025, and 0.002 inch respectively. The weights of these wires are approximately 0.00182, 0.0013, and 0.00081 gramme respec-

* Phil. Trans. A. 1887.

tively, whence, taking the specific heat of platinum as 0.037, the thermal capacities are 0.0000673, 0.0000481, and 0.00003 gramme-degrees respectively.

I had intended to measure the temperatures by means of all three wires, and from the results obtain a curve giving the lag of the wires; this was, however, not possible owing to want of time and apparatus, but the two finer wires gave temperatures which were nearly equal, while the coarser wire gave results somewhat lower than the two others. This induced me to work with the 0.0025 wire for the bulk of the experiments, as the 0.002 wire had so little mechanical strength that, if an abnormal explosion occurred, it was invariably destroyed.

Calibration of the Thermometers.

The ice points call for no special remark beyond the fact that, in spite of considerable care in ensuring a mixture of finely crushed ice and water, they were by no means as satisfactory as the steam points. The average resistance of the 0.003, 0.0025, and 0.002 inch diameter wires was 0.3, 0.55, and 0.75 ohm respectively. The steam points were obtained in a double-jacketed hypsometer of the ordinary form, and were corrected for barometric pressure when necessary. When working with these very fine wires, it is imperative to guard against the heating effect of the battery current, otherwise discrepant and inaccurate results are obtained. I have found that the Daniell cell, mentioned above, with resistance in the external circuit gave no appreciable heating unless the observations were made too rapidly. (This of course only applies to the ice and steam points; when in the engine battery heating is of no importance.)

Two methods were used to obtain the quantity δ . The first method was a comparison of the fine-wire thermometer with a standard Callendar platinum thermometer, both being placed in a tube heated to a high temperature, thus getting a third point on the curve connecting the air and platinum scales.

The standard thermometer consisted of a spiral of platinum

wire of a diameter of 0.008 inch wound on a flat plate of mica and enclosed in a porcelain tube 50 centimetres in length, the flat spiral occupying a length of about 7 centimetres from the closed end of the platinum tube. The fixed points of this thermometer were determined many times in ice and steam, and several times in sulphur and aniline vapours. The values were

$$R_0 = 2.936 \text{ ohms,}$$

$$R_1 = 4.080 \text{ ohms,}$$

$$\delta = 1.52.$$

I have not been able to detect any change in the zero, although this thermometer has been raised to a bright red heat several hundred times during the last two years.

For the comparison of the two thermometers an ordinary gas-furnace, such as is used for combustion work, was first used, but was abandoned owing to unequal and unsteady heating. After some trials I adopted a tube-furnace heated with gas-coke; from end to end of the furnace (about 2 feet in length) was placed a cast-iron tube $2\frac{1}{2}$ inches diameter outside and $\frac{1}{2}$ inch thick. This tube could be rotated in bearings, and thus the temperature could be kept steady round the circumference. Inside the cast-iron tube, and independently supported, was a thick copper tube in which were placed the two thermometers for comparison, the fine wire of the steel-tube thermometer nearly touching the porcelain tube of the standard. Owing to the great mass of the metal, the temperature in the inner tube changed very slowly, and by regulating the draught a temperature of 500° to 600° C. could easily be obtained. Although this was much better than the gas-furnace, as regards an equal temperature circumferentially, still it could not be assumed that the whole length of the coil of the standard thermometer was at the same temperature as the fine wire on the steel-tube thermometer. During any comparison the standard did not show a variation of more than 2° C. Unfortunately the fine wire having such a small thermal capacity as compared with the standard, may not be at quite the same temperature as the standard if there is even the slightest change in the

temperature. For these reasons the values of δ as determined by this method are not so satisfactory as might be wished.

In the second method the resistance of the steel-tube thermometer was determined in sulphur vapour as well as in ice and steam. The sulphur was boiled in an apparatus similar to the first form used by Callendar and Griffiths in their determination of the boiling-point of sulphur*. This consisted of a boiler and condenser made of iron tubes. While this method gives very accurate and satisfactory results, it requires extreme care and takes several hours to obtain a steady temperature.

Results of the Experiments.

It was not until the summer of 1894 that I was able to make any proper experiments with the wires in the cylinder of the gas-engine. I directed my attention at first to the determination of the best speed for the engine, and to find what conditions were necessary to obtain regularity and to ensure that the measuring-wire should follow the temperature of the expanding gases. I found that to obtain regular and perfect combustion of the gases, the water-jacket of the cylinder had to be kept at a temperature of from 50° to 60° C., otherwise abnormal explosions were frequent. The speed of the engine was kept constant at about 120 revolutions per minute, and the wire was found to follow the cycle at this speed except at the beginning of the stroke. The number of explosions per minute was from 12 to 14, each explosion being followed by about 20 blank strokes. The effect of the thorough "washing-out" of the products of combustion from the cylinder and of the hot cylinder jacket was to produce a temperature in the cylinder as high as, if not higher than, if the engine had been working at full load. The small number of working strokes per minute enabled observations to be made with the galvanometer which would not have been possible at much closer intervals of time. The wear and tear on the measuring-wire was reduced, it being a matter of considerable importance to expose the wire to as few explosions as possible.

* Phil. Trans. A. 1891.

In all the following experiments the thermometer measuring-wire was placed on the axis of the cylinder and in the centre of the compression space.

Two thermometers were used, both practically of identically the same construction as described above. The results of a number of experiments are given below; I have selected those which I have reason to believe are the most complete and accurate of the number which I have made. Wherever I have been able, I have given the constants of the thermometers which were determined before and after the experiments; where it is not given it is because the wire fused before a re-calibration could be made.

January 1st, 1895.

Thermometer No. 5. Wire 0.003 inch diam.
Air temperature 9° C. Circulating water, 46° C.

R_0 before, 0.324 ohm. $R_1 - R_0 = 0.1206$. $\delta = 1.52$.
 R_0 after, 0.340 ohm.

First Set.			
Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temperature on air-scale.
10	1.476	948	1120
20	1.443	921	1085
30	1.433	913	1070
40	1.362	854	990
50	1.351	845	975
60	1.299	802	925
70	1.286	791	900
80	1.238	751	850
Second Set.			
10	1.547	1007	1210
20	1.477	949	1120
30	1.466	940	1110
40	1.433	921	1085
50	1.382	871	1010

It will be noticed that the second set show considerably higher temperatures than the first; this is due to the fact that the former set were taken just before darkness came on,

and the second after the gas-pressure had risen considerably. Owing to this I have generally worked in the morning, when the gas-pressure is generally steady except when there is a sudden fog.

January 2nd, 1895.

Thermometer No. 4. Wire 0.0025 inch diam.

Circulating water 50° C.

R_0 before, 0.5216 ohm. R_1 before, 0.7153 ohm. δ before, 1.397.
 R_0 after, 0.5357 ohm. R_1 after, 0.7328 ohm. δ after, 2.09.

Percentage of stroke.	Observed Resistance, ohms.	pt.	Temp. on air-scale. $\delta=1.74$.
10	2.474	998	1245
20	2.455	988	1230
30	2.366	942	1150
40	2.306	912	1120
50	2.248	882	1060
60	2.128	820	970
70	2.108	810	950

January 4th, 1895.

Thermometer No. 4. Wire 0.0025 inch diam.

Air temperature 10° C. Circulating water 55° C.

$R_0=0.530$. $R_1-R_0=0.1971$. $\delta=1.74$.

Percentage of stroke.	Observed Resistance, ohms.	pt.	Temperature on air-scale.
Explosion	2.414	956	1189
10	2.483	988	1230
20	2.439	965	1195
30	2.356	923	1130
40	2.338	914	1120
50	2.256	873	1040
60	2.184	836	990
70	2.094	790	920
80	1.960	722	830

Thermometer No. 5. Wire 0·003 inch diam.

$$R_0 = 0\cdot332. \quad R_1 - R_0 = 0\cdot1206. \quad \delta = 1\cdot52.$$

Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temperature on air-scale.
Explosion	1·444	919	1080
10	1·476	949	1120
20	1·451	928	1095
30	1·439	918	1080
40	1·395	818	1025
50	1·392	879	1020
60	1·333	830	955
70	1·268	776	880
80	1·238	751	855

No further experiments were made with this wire as is clearly did not attain the proper temperature.

January 31st, 1895.

Thermometer No. 4. Wire 0·0025 inch diam.

Air temperature 7·5° C. Circulating water 57° C.

$$\begin{array}{lll} R_0 \text{ before, } 0\cdot562 \text{ ohm.} & R_1 - R_0 \text{ before, } 0\cdot220 \text{ ohm.} & \delta \text{ before, } 1\cdot90. \\ R_0 \text{ after, } 0\cdot581 \text{ ohm.} & R_1 - R_0 \text{ after, } 0\cdot227 \text{ ohm.} & \delta \text{ after, } 1\cdot90. \end{array}$$

Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temperature on air-scale.
10	2·562	893	1100
20	2·595	907	1125
30	2·524	876	1080
40	2·445	840	1020
50	2·360	802	960
60	2·338	792	940
70	2·186	729	850
80	2·151	711	825

February 12th, 1895.

Thermometer No. 5. Wire 0·002 inch diam.

Air temperature 7° C. Circulating water 43° C.

$$R_0 \text{ before, } 0\cdot796 \text{ ohm.} \quad R_1 - R_0 = 0\cdot283 \text{ ohm.}$$

Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temp. on air-scale. δ = 1·22.
10	3·662	1012	1160
20	3·616	996	1140
30	3·477	947	1075
40	3·352	907	1020
50	3·253	868	970
60	3·120	821	910
80	3·071	804	890

This wire was destroyed by accident during my absence before a new value of δ could be determined.

Thermometer No. 4. Wire 0.0025 inch diam.

$$R_0 = 0.592. \quad R_1 - R_0 = 0.223. \quad \delta = 1.90.$$

Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temperature on air-scale.
Explosion	2.529	878	1080
10	2.580	891	1100
20	2.576	890	1100
30	2.499	855	1040
40	2.459	837	1010

The wire partly fused during the observation at 50 per cent. These experiments were made during a period of intense cold, and the indicator diagrams showed the pressures to be lower than usual. The temperatures were lower than those of Jan. 1-5 or March 7-20, otherwise the fine wire on thermometer No. 5 would not have remained intact so long.

March 7th.

Thermometer No. 4. Wire 0.0025 inch diam.

Air temperature 10° C. Circulating water 46° C.

R_0 before, 0.537 ohm. $R_1 - R_0$ before, 0.208. δ before, 1.81.
 R_0 after, 0.551 „ $R_1 - R_0$ after, 0.208. δ after, 1.75.

Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temp. on air-scale. $\delta = 1.78.$
10	2.437	913	1115
20	2.450	920	1120
30	2.381	886	1090
40	2.333	861	1060
50	2.304	849	1015
70	2.204	801	940
80	2.113	757	880

March 16th.

Thermometer No. 4. Wire 0.0025 inch diam.
 Air temperature 13° C. Circulating water 50° C.

R_0 before, 0.551 ohm. $R_1 - R_0 = 0.207$.
 R_0 after, 0.551 ohm. δ (determined by sulphur vapour) 1.75.

Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temperature on air-scale.
10	2.434	909	1100
20	2.354	870	1045
30	2.364	875	1050
40	2.236	833	990
60	2.163	778	910
70	2.057	727	840

I was so doubtful of the second and third points that I repeated the first three with the results below :—

10	2.452	917	1115
20	2.373	879	1055
30	2.369	877	1050

March 20th.

Same thermometer and wire.
 Air temperature 13° C. Circulating water 51° C.

Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temperature on air-scale.
10	2.481	931	1140
20	2.403	894	1080
30	2.403	894	1080

The temperature was variable throughout this experiment and the wire fused during the observation at 40 per cent.

I consider these experiments to be the most accurate of the whole series.

Towards the end of February I determined to find δ by means of an observation in sulphur vapour; and as some question had arisen as to the action of the high-temperature gases on the platinum wires, more especially as to the variation of the quantity δ , I gold-soldered a platinum wire 0.002 diameter on No. 5 thermometer, and determined its fixed

points and calculated the δ before this wire was placed in the engine. In every other case the wires had been exposed to the action of the cylinder gases for about half an hour before the determination of the fixed points. In this case the wire had only been exposed to the flame of the blowpipe used in the soldering. The fixed points were $R_0=0.7596$; $R_1=1.0536$; $\frac{R_1}{R_0}=1.32$; $R_1-R_0=0.294$; $\delta=2.93$.

This value of δ seemed so high that I repeated the whole of the points without detecting any error in the previous work. The low value of $\frac{R_1}{R_0}$ together with the high δ seems to indicate that a gold-platinum alloy formed at the junction of the main lead to the fine wire and on the surface of the latter. The thermometer was then placed in the engine on March 16th and gave the following results :—

Percentage of stroke.	Observed Resistance, ohms.	<i>pt.</i>	Temperature on the air-scale.
10	3.527	948	1200

After running in the engine some time the fixed points were re-determined with the results given below :—

$$R_0=0.786. \quad R_1=1.075. \quad R_1-R_0=0.289.$$

$$\frac{R_1}{R_0}=1.37. \quad \delta=1.95.$$

From this it will be seen that the action of the gases on the cylinder had been such as to bring the wire into a normal condition, most probably by sweeping off any alloy which had been formed.

I have plotted the results of the experiments, and the curves are given in Plate XI. figs. 5, 6, & 7, the corresponding pressure-volume curves being given in figs. 8, 9, & 10. In figs. 5, 6, & 7 the horizontal ordinates show the percentage of the stroke, and the vertical ordinates the temperature in degrees C. on the air-scale, the observed points being marked by small circles. I have divided the experiments up into three groups—the first being from Jan. 1 to Jan. 4, the second from Jan. 31 to March 7, and the last from March 16 to March 20. It will be noticed that those of Jan. 1–4 (fig. 5) show a distinct break in the regularity of the curve, the line falling but little

between the 3rd and 4th points on the 0.0025 wire and between the 4th and 5th points on the 0.003 wire, instead of falling regularly throughout as would have been expected. The curves of the second group of experiments (fig. 6) show no trace of irregularity ; while those of the third group (fig. 7) show a strongly marked variation between the 2nd and 3rd points. Several explanations of this singularity have suggested themselves to me, but I do not consider them to come within the scope of this paper. I hope to make further experiments bearing on this matter, and to obtain more data on the subject. The results of the experiments of Jan. 31 to March 7 are chiefly interesting as showing the close concordance of temperatures registered by wires of such different thermal capacity, especially when it is remembered that the source of heat used was a very variable one, the pressures, as shown on the indicator cards, varying from day to day, and also during the day, owing to the varying gas-pressure and quality.

I would also point out that a difference of 100 degrees shown on the thermometers corresponds to a distance of about $\frac{1}{2}$ inch on the indicator cards.

In conclusion I must express my thanks to Messrs. Johnson and Matthey for the trouble they have taken in drawing down the wires, several of which were of special diameters. I should have been quite unable to carry out costly experiments of this kind had it not been for the liberality of my brother, Mr. H. R. J. Burstall, who has provided me with the necessary funds. The apparatus has been designed and carried out in conjunction with him ; and I wish to express my sincere indebtedness to him for his many suggestions, which have made these experiments possible.

DISCUSSION.

Prof. PERRY said that an instrument for quickly recording varying temperatures was greatly required by engineers. The temperature just inside the cylinder-walls was, however, most important to determine ; and a knowledge of how the temperature from 1 to 2 mm. inside the walls varied would be of the greatest value. He would like to ask the author if the observed temperatures agreed with the values calculated

on the assumption that the gases in the cylinder behaved as a perfect gas, and that

$$\frac{PV}{T} = \text{constant}$$

during the whole stroke. Differences between the observed and calculated values might be due to dissociation, and not entirely to lag in the thermometers. It was astonishing that even the fine wires employed were able to follow the rapidly varying temperature, and he would like to see some special experiments made to test this point.

Prof. CAPPER showed a diagram giving the values calculated on the assumption that

$$\frac{PV}{T} = \text{constant}.$$

In such a calculation it was necessary to assume some temperature as a starting point, and in general this temperature was obtained from an analysis of the exhaust gases, so that the calculated curve is most likely to depart from the truth at the commencement of the stroke. He (Prof. Capper) hoped that the author would be able to accurately determine the temperature of some one point of the stroke, and he suggested that the point where the observed curve crossed the theoretical curve would be the most suitable one for this purpose. Such a point must exist, since at the commencement of the stroke the lag causes the observed temperature to be too low, while at the end of the stroke the observed temperatures are too high. Mr. Burstall finds a curious bump in his curves, and it is curious that a similar bump exists in the calculated curves. From the constancy with which this bump appears, it would seem that it must have some physical meaning. It was important to remember that the expansion of the gas-engine cylinder is not adiabatic, for heat is both abstracted and generated during the stroke.

Mr. BLAKESLEY suggested that since the temperatures dealt with were sufficient to make the wire red-hot, the question of lag might be investigated by means of Becquerel's phosphoscope at a known interval after the removal of the source of heat.

Mr. GRIFFITHS said he considered an important source of

error was the large thermal capacity of the leads when the working wire was so very short. He thought it would be possible to standardise the thermometers under conditions somewhat similar to those which occur in the engine cylinder. Thus, perhaps alternate gushes of air at 0° and 100° C. might be used. The use of gold to attach the fine wire to the leads was objectionable, since the gold must permeate the platinum for quite an appreciable fraction of the whole length of the wire. He would like to know whether the change in δ alluded to by the author occurred with the first explosion or whether it was a gradual one.

Mr. ENRIGHT pointed out that the nature of the working substance in a gas-engine varied during the stroke.

Prof. PERRY said that the change in the specific volume of the gases before and after combustion did not amount to more than 1.25 per cent.

Mr. E. WILSON said he thought it was most important to shorten the time of contact, since at present the galvanometer readings corresponded to the mean temperature over a range of about 5 per cent. of the whole stroke. It might be possible to make use of a condenser to get over this difficulty.

Prof. RÜCKER said that the Kew Observatory were making arrangements to undertake the testing of platinum thermometers.

Mr. ENRIGHT suggested that with a very short contact induced currents might cause errors.

Mr. RHODES said he had found that the method of determining the zero-point of thermometers by means of melting ice was far from satisfactory, and that the results obtained could not be depended upon to within $0^{\circ}.1$ C.

The AUTHOR, in his reply, said the only chemical action on the wires he thought probable was the formation of a carbide. After several hours' use, however, the wires appear quite bright and clean.

L. *A New Method in Harmonic Analysis.**By* ARCHIBALD SHARP.*

[Abstract.]

THE author, in this paper, applies the principle of the form of harmonic analyser for giving direct readings of the amplitude and epoch of the various constituent harmonic terms previously described by him, to the performance of harmonic analysis without the use of an instrument. The kinematic principle is as follows:—Let the curve to be analysed be drawn, with a scale of abscissæ such that the period is 2π . Let a wheel, w , roll on the paper and be connected with a tracing-point, P , in such a manner that as P moves uniformly in the x direction the axis of the wheel w turns uniformly counter-clockwise in a horizontal plane, and the distance rolled through during any short interval is equal to the corresponding displacement in the tracer P in the y direction. The curve traced out by w the author calls the roller curve, and from the vector joining the initial and final points of this curve the amplitude and epoch can be determined. Suppose the periodic curve consists of a portion of the curve,

$$y = a_0 + a_1x + a_2x^2 + a_mx^m,$$

repeated over and over again; then if the tracer is taken round this periodic curve you get a rolled curve, which may be called the first rolled curve. If now the curve whose ordinates are

$$\frac{dy}{dx}$$

is traced out, the roller curve obtained is the evolute of the first, and so on for

$$\frac{d^2y}{dx^2}, \text{ \&c.}$$

The author gives two worked examples, and compares the values of the coefficients obtained with those given by the harmonic analyser of the Guilds Central Technical College.

* Read May 10, 1895.

LI. *The Thermal Constants of the Elements.**By* N. F. DEERR.*

[Abstract.]

THE author has found that there is considerable evidence in favour of the following relations existing between one metal and another, or between one non-metal and another, in any group of elements in the periodic classification.

1. $(T + L/S)C = \text{const.}$ 2. $T.C = \text{const.}$ 3. $L.C/S = \text{const.}$; where T denotes the absolute temperature of fusion ; L the latent heat of fusion, per unit mass ; S the mean specific heat between the absolute zero and the melting point ; C the mean coefficient of expansion between the same units.

On the opposite page is a chart of the periodic classification of the elements with values of the quantities mentioned above, so far as they can be calculated with the present available data ; in the absence of other data the values of S and C have been taken between 0° C. and 100° C.

It will be seen on reference to the annexed table that whereas in the majority of cases the agreement is most striking, the only entirely discordant element is mercury. In the eighth group the three or four elements in one horizontal line agree, this being particularly marked in the values of T.C ; these values, however, decrease slightly in passing down from one series to another.

The author obtained the first relation by assuming the total heat of liquefaction of unit mass and the heat required to expand unit mass of that body through any fraction of its initial length to be directly proportional to intermolecular attraction : the second and third relations were obtained by combining the first relation with one recently brought forward before the Chemical Society by Mr. Holland Crompton (Trans. cxlv. p. 240) :— $A \cdot L/T = \text{Valency} \times \text{Const.}$, where A denotes the atomic weight ; in this way the first relation may be considered as composed of the second and third.

All the data used are to be found in Landolt and Börnstein's Tables and in Dammer's 'Inorganic Chemistry,' with the exception of these latent heats :—Sodium and Potassium, Joannis ; Gold, Rose ; Aluminium, Richards ; Thallium, Neville and Heycock.

* Read June 14, 1895.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.			
	Li.	Be.	B.	C.	N.	O.	F.				
	Na.	Mg.	Al.	Si.	P.	S.	Cl.				
T+L/S)C...	·0337	...	·0231	...	·042	·0278	...				
T.C	·0260	·0207	·0201	·0112	·039	·0246	...				
L.C/S	·0077	...	·003	...	·003	·0032	...				
	K.	Ca.	Sc.	Ti.	V.	Cr.	Mn.	Fe.	Co.	Ni.	...
T+L/S)C...	·0359	·0254
T.C	·0280	·0228	·022	·021	...
L.C/S	·0079	·0026
	Cu.	Zn.	Ga.	Ge.	As.	Se.	Br.				
T+L/S)C...	...	·0278	·146				
T.C	·0248	·0192	·0038	·0217	·093				
L.C/S	·0086	·053				
	Rb.	Sr.	Yt.	Zr.	Nb.	Mo.	...	Ru.	Rh.	Pd.	...
T+L/S)C...	·0263	...
T.C	·0199	·0193	·0191	...
L.C/S	·0072	...
	Ag.	Cd.	In.	Sn.	Sb.	Te.	I.				
T+L/S)C..	·0319	·0276	...	·0210	·142				
T.C	·0244	·0194	·0193	·0141	·0081	·0127	·091				
L.C/S	·0075	·0082	...	·0070	·051				
	Cs.	Ba.	Di.	Ce.				
				
	Er.	La.	Ta.	W.	...	Os.	Ir.	Pt.	Au.
T+L/S)C...	·0256	·0263
T.C	·0182	·0173	·0180	·0190
L.C/S	·0076	·0073
	...	Hg.	Tl.	Pb.	Bi.				
T+L/S)C...	...	·0191	·0225	·0210	·0129				
T.C	·014	·0173	·0163	·0071				
L.C/S	·0051	·0052	·0047	·0058				

LII. *The Thermal Properties of Isopentane.*

By SYDNEY YOUNG, *D.Sc., F.R.S., University College, Bristol.*

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INTRODUCTION.

THE relations between the temperatures, pressures, and volumes of gases and liquids have been the subject of numerous experimental and mathematical investigations since the publication of the classical experimental researches of Andrews, and the great mathematical investigation of van der Waals on the continuity of the gaseous and liquid states of matter. Among the substances which have been most thoroughly studied are the elementary gases—oxygen, nitrogen, hydrogen; a few compounds which are gaseous under ordinary conditions, such as carbon dioxide and ethylene; and a few liquids, especially ether, the lower alcohols, and water.

The experiments on oxygen, hydrogen, and nitrogen have necessarily been chiefly carried out at temperatures far above their critical points, whilst with ethylene and carbon dioxide the range of temperature below the critical temperature at which observations have been made is small. It is also, as a rule, more difficult to fill a tube with a gas in a perfectly pure state than with a liquid.

Of the liquids examined, the alcohols and water behave abnormally in many respects, owing probably to the existence of complex molecules in the liquid state; and though the results obtained are of great interest, it is obvious that a thorough investigation of what may be termed normal substances should be carried out before the behaviour of such abnormal compounds can be properly understood.

None of the substances yet examined have given better results than ethyl ether. It can be obtained without great difficulty in a state of purity; it is possible to obtain results through a considerable range of temperature both above and

below its critical temperature, and its critical pressure is moderately low.

Experiments on ether over a wide range of volume and temperature have been made by Ramsay and Young (Phil. Trans. 1887, A, p. 57), and also by Battelli (*Mem. della R. Ac. di Torino*, [2] xl. 1889), and up to extremely high pressures—though with a small range of volume—by Amagat (*Annales Chim. Phys.*, series 6, vol. xxix.), and by Barus (Phil. Mag. 1890, vol. xxx. p. 358).

The result of these investigations is to show that although the formula of van der Waals, $\left(p + \frac{a}{v^2}\right)(v-b) = RT$, gives the general form of the isothermal curves very satisfactorily and, indeed, agrees well with the experimental results at large volumes, yet it cannot be regarded as sufficiently accurate at volumes near and below the critical volume.

At constant volume, however, since $\frac{a}{v^2}$ and $(v-b)$ are both constants, the formula of van der Waals may be reduced to the form $p = bT - a$, where a and b are constants depending on the nature of the substance and on the volume*.

This relation was found to hold good by Amagat (*Comptes Rendus* (1882), xciv. p. 847) in the case of carbon dioxide and ethylene in the gaseous state and approximately in the liquid state, and by Ramsay and Young (Phil. Mag. May 1887, p. 435) in the case of ether in both the gaseous and liquid states.

Barus (*loc. cit.*) has shown that the law holds good for ether and some other substances in the liquid state up to a pressure of 1000 atm., but that there are deviations at higher pressures. Up to 1000 atm. he estimates the error as not greater than 2 or 3 degrees.

Further investigations by Ramsay and Young (Phil. Mag. August 1887, p. 195) have shown that the law is applicable, approximately at any rate, to methyl and ethyl and (Phil. Trans. 1889, A, p. 137) propyl alcohol, but that there are

* The symbols b and a in the equation $p = bT - a$ have, of course, not the same meaning as in van der Waals's equation, but as they have been used in previous papers by Ramsay and myself I have thought it best to adhere to them.

considerable deviations in the case of water (Phil. Trans. 1892, A, p. 107).

Further experiments—up to very high pressures, though with a small range of volume—have been carried out by Amagat (*Ann. Chim. Phys.* loc. cit.), and his conclusions will be referred to later.

The number of substances that can be conveniently investigated through a sufficiently wide range of temperature both above and below the critical temperature and through a wide range of volume (in both the gaseous and liquid states) is very limited; it therefore seemed desirable to take advantage of the opportunity, afforded by the possession of a quantity of pure isopentane, to make as complete an investigation as possible of the relations between the temperature, pressure, and volume of this substance. It would be difficult to find a more suitable liquid; it is extremely stable and is readily freed from moisture by distillation over phosphorus pentoxide; its boiling-point is $27^{\circ}.95$; its critical temperature is $187^{\circ}.8$, and its critical pressure 25020 millim.

EXPERIMENTAL RESULTS.

Preparation of Pure Isopentane.

A quantity of "pentane" was procured from C. A. F. Kahlbaum of Berlin, who has kindly informed me that the substance is obtained as a bye-product in the preparation of amylene from amyl alcohol, the admixed amylene being separated by means of bromine. The isopentane was shaken with concentrated sulphuric acid and afterwards repeatedly with a mixture of concentrated sulphuric and nitric acids. The action in each case was at first somewhat violent, but it moderated after several additions of the acids had been made.

After standing all night over sulphuric and nitric acids the isopentane was again repeatedly shaken with sulphuric acid—which was at first coloured a deep orange; it was then treated with a strong solution of potassium hydrate, washed with water, dried with solid potassium hydrate, and distilled*.

* It is possible that the substance might have been satisfactorily purified by treatment with bromine. The loss by evaporation would probably have been smaller and the process less troublesome.

PHYSICAL SOCIETY OF LONDON.

ABSTRACTS OF PHYSICAL PAPERS FROM FOREIGN SOURCES.

OCTOBER 1895.

GENERAL PHYSICS.

645. *Osmotic Pressure.* **Ponsot.** (Bull. Soc. Franç. Phys. No. 62, 1895.)—The author discusses the relation of the theory of Leduc's method for determining osmotic pressure (Abstracts 340, 483) to that of the usual methods by the lowering of the freezing-point or by diminution in vapour-pressure of the solution. S. S.

646. *Humidity on the Sonnblick.* **J. Hann.** (Wien. Ber. 104. 4. Part IIa. pp. 351-401, 1895.)—Since September 1893 a new type of Richard recording hygrometer, the membrane of which is replaced by hair, has been used on the Sonnblick, at an altitude of 3100 m. The instrument agrees well with Koppe hair-hygrometers and psychrometers, and has been controlled by comparative observations taken on the Theodulpass, 3300 m. high. Psychrometers, as yet chiefly employed for such work, even if fitted with Ekholm's improvements, would hardly be suitable on the Sonnblick, where the thermometer rarely rises above zero. The humidity does not vary with the seasons on high mountains as it does in low lands; on the Alps the minimum occurs in winter, the maximum in spring and summer. The dry winter has the least periodic diurnal amplitude, but the greatest aperiodic, irregular variations. Apart from the winter months, the minima take place between 7 and 10 A.M.; during the later evening hours the humidity attains its maximum. In winter the moisture percentage is below the mean between 6 P.M. and 7 A.M.; the maximum occurs about or after noon, the minimum in the early hours of the night. The great

dryness of the night is connected with the radiation from the higher mountains producing down-currents into the valley and a sinking of higher, drier strata on to the summits. The vapour-tension curves follow, on the whole, the temperature-curves on mountains as in the valleys. But the relative moisture also follows, in its daily variations, the temperature on the peaks, lagging noticeably behind; whilst at lower elevations the relative humidity decreases with increasing temperature. The driest hour precedes the most serene hour; in the afternoon the ascending warm currents increase the moisture. Very peculiar are, on the Sonnblick, the sudden decreases in moisture, which appear confined to the winter. Thus, in October 1893, 90 per cent. of relative humidity was registered at midnight, 50 per cent. at 1 A.M., 24 per cent. at 7 A.M. Such periods are accompanied by a rise of the thermometer and the barometer, and occur in areas of barometric maxima. Very dry days were observed: 32 in winter, 10 in spring, 4 in summer, 15 in autumn.

The paper contains many tables, the most complete records of continued observations at high altitudes, and frequent references to observations made on the Faulhorn, Grands Mulets, Ontake (Japan), etc.

H. B.

647. *Water in Atmosphere of Mars.* **J. Janssen.** (C. R. 121. pp. 233-237, 1895.)—In consequence of observations made at the observatory on Mount Hamilton, W. W. Campbell came to the remarkable conclusion last year that no aqueous vapour is contained in the atmosphere of Mars. Various discussions have taken place, and, as a result, Campbell, in an article contained in last June's number of the 'Astrophysical Journal,' expressed a desire to know more details of Janssen's observations published in 1867: hence the article under consideration.—In 1862 Janssen discovered the spectroscopic bands caused by aqueous vapour in our earth's atmosphere, without knowing the earlier observations made by Brewster in 1833. From the 12th to the 15th of May, 1867, after having previously familiarised himself with the bands due to aqueous vapour, he made observations on the summit of Etna: on the 13th Mars had, on crossing the meridian, an altitude of 72° , and at sunset, when the observations commenced, one of more than 60° . The cold was excessive, and the quantity of vapour in the earth's atmosphere was very small—not enough to make visible group C, and still less group D. The moon, which was lower in the heavens than Mars, furnished an excellent means of comparison. When Mars was examined, groups C and D, although feeble, were distinctly visible. It was in consequence of this observation, confirmed afterwards at Palermo and Marseilles, that Janssen announced the presence of the vapour of water in the atmosphere of Mars. He will publish later some observations of the same kind which have been made since 1867.

A. Gs.

648. *Refractive Equivalent of Oxygen, Sulphur, and Nitrogen.* **R. Nasini** and **G. Carrara.** (Zschr. phys. Chem. 17. pp. 539–544, 1895.)—The compounds which have been examined are those which contain the above elements as part of their closed ring-nucleus. The authors calculate the molecular refraction, using both Gladstone's and Landolt's formula. They find that these elements have different values in the substitution-derivatives of the compounds: thus in furfuran the value for oxygen is 0.46, whilst in dimethyl-furfuran it is 1.55. The results for seventeen compounds are stated in a table. S. S.

649. *Action of Infra-Red Rays on Silver Sulphide.* **H. Rigollot.** (C. R. 121. pp. 164–166, 1895.)—The author forms what he calls an electrochemical actinometer, by placing in a saline solution two plates of silver covered with sulphide, which are connected to a Lippmann electrometer, a Thomson galvanometer of high resistance, or some such apparatus. When infra-red or other rays strike one of the plates it always becomes negative with respect to the other, whatever be the solution employed. The difference of E.M.F. is developed instantly. In order to test whether the action is actinic or thermal, the author placed two plates in a sort of U-tube, and the liquid (a solution of sodium chloride) was heated: a rise in temperature of 6° or 7° was necessary to produce an E.M.F. of two-thousandths of a volt; light equal in intensity to that caused by a Carcel lamp placed at a distance of 20 cm. was necessary to produce the same E.M.F. Solutions of NaCl, NaBr, NaI, KBr, KI, K₂SO₄, MgSO₄, AgSO₄, C₂H₃AgO₂ were experimented with. The illuminated plate was always negative with respect to the other; whilst the heated plate was negative with solutions of salts of silver, and positive with all the other salts examined. A. Gs.

650. *Kinetic Theory of Gases.* **S. Blaserna.** (Rend. Acc. Linc. 4. 1. pp. 315–318, 1895.)—Recent investigations of Amagat on the compressibility of anhydrous carbonic acid show that, if we use (pv) for ordinate and v for abscissa, the isothermals are approximately parabolas. Signor Blaserna shows that this result may be deduced from van der Waals' formula

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT,$$

without any assumption regarding the constants a and b .

The treatment of this equation is simplified by using v for independent, and (pv) for dependent variable. For we have

$$(pv) = \frac{RTv - a + \frac{ab}{v}}{v - b};$$

and making (pv) minimum, we get

$$v^2 - \frac{2b}{1-\tau} v = -\frac{b^2}{1-\tau},$$

in which

$$\tau = \frac{b}{a} RT,$$

a quantity proportional to the absolute temperature.

Solving this quadratic, and observing that both p and v , and therefore pv , must be positive, we obtain the three equations

$$v = \frac{b}{1 - \sqrt{\tau}},$$

$$(pv) = \frac{a}{b} (2\sqrt{\tau} - 1),$$

$$p = \frac{a}{b^2} (3\sqrt{\tau} - 2\tau - 1),$$

all of which are positive if $\tau > \frac{1}{4} < 1$. Giving to τ successively the values .25, .3, &c., he obtains numerical values for $\frac{v}{b}$, $\frac{b}{a} pv$, and $\frac{b^2}{a} p$. If

$$y = 2\sqrt{\tau} - 1,$$

$$x = 3\sqrt{\tau} - 2\tau - 1,$$

and we eliminate τ , we obtain

$$x = \frac{1}{2}y - \frac{1}{2}y^2,$$

which is a parabola.

S. H. B.

651. *Automatic Mercurial Air-Pump.* **F. Neesen.** (Wied. Ann. 55. pp. 732-736, 1895.)—The instrument described, akin to Geissler's, may be called a reservoir-pump; it is worked by an auxiliary water-pump. The mercury is raised and lowered in the reservoir by the automatic motion of two valves which allow the mercury in the cistern to be exposed to the atmospheric pressure, or freed from it by the action of the auxiliary pump. The peculiarity of the automatic valve-motion is that the valves are moved by a system of floats, of which one part varies its weight by admission and recess of mercury, so that there is the necessary difference of level in the cistern between the phases of valve-opening and closing, corresponding to whether the mercury is rising or falling. The adjustment for preventing too rapid rise of mercury as the pressure falls below 1 mm. is made by withdrawing a little mercury from the cistern into a side vessel. The author describes an arrangement with a tap instead of valves, the difference of phase in action being effected by an automatic variation of the leverage acting on the tap.

A. Gs.

652. *Velocity of Projectiles.* **A. C. Crehore** and **G. O. Squier.** (Phys. Rev. 3. pp. 63-70, 1895.)—The paper contains an account of an application of a new polarising photo-chronograph to the measurement of the velocity of projectiles. The instrument consists of a camera and a modification of the apparatus described in Trans. Am. Inst. El. Eng. vol. xi. No. 10, by A. C. Crehore. White light is passed through a polariser, then through a transparent substance possessing the property of rotating the plane of polarisation when in a magnetic field, and then through an analyser. The polariser and analyser are crossed so that no light passes through when the transparent substance (carbon bisulphide) is not subjected to the influence of a magnet. The tube containing the carbon bisulphide is surrounded by a coil of wire; when a current flows the plane of polarisation is rotated, and light passes through the analyser and is caught on a photographic plate. The projectile makes the electric circuit as it passes through screens at a known distance apart, and the time is measured in much the same way as in determining the value of " g " with an electrical chronograph.

W. G. R.

653. *Curvimeters.* **E. Hammer.** (Zschr. Instrumk. 15. pp. 278-280, 1895.)—Reference is made to two instruments which have recently been set up at the University of Stuttgart by Dr. W. Ule. The first is a "parallel curvimeter" (German Patent No. 79948), and the second is a "polar curvimeter." No details of the mechanism are given.

R. A.

654. *Matches.* **T. Schloesing.** (C. R. 121. pp. 331-336, 1895.)—As there is still a preference in France for matches which strike anywhere, whilst the use of yellow phosphorus is to be deplored, the Government have nominated a Committee, consisting essentially of members of the Academy, to report on explosive pastes. Many of the specimens submitted strike even on cloth, though not so readily as the ordinary lucifer, and can be manufactured without danger; but they are apt to catch fire by accidental friction. The author finds that both chlorate of potash and red phosphorus are indispensable. He generally admixed sand or powdered glass, and gum or glue, and, further, sulphur, antimony sulphide, or hyposulphite of lead. Nitrates, oxidised minium (minium treated with nitric acid—a mixture of nitrate and peroxide), peroxide of lead, manganese dioxide, chromates, and bichromates will not light by friction, even when mixed with amorphous phosphorus. To light on rubbing, a safe paste should, in the dry state, contain 12 or 15 per cent. of red phosphorus and not more than 35 of chlorate; the exact proportions must be left to the manufacturer, as too much depends upon the state of subdivision. The author has further investigated the combustion products, which may become dangerous when thousands of matches catch fire, which is not a rare case in works. He prepared a bell, in which by means of a hot wire he lighted 25 matches at the

time, withdrew the matches, and introduced another batch after half an hour, until a hundred matches had been burnt. Six kinds were tested, all containing red phosphorus and, besides, either persulphide of antimony or hyposulphite of lead, or both together. In the liquid obtained by rinsing the bell he found from 23 to 98 per cent. of the phosphorus, as phosphoric acid, up to 31 of the lead as white oxide, and 39 per cent. of the antimony as acid. No further tests are mentioned.

H. B.

655. *Comparison of Automatic Air-Pumps.* **F. Neesen.** (Zschr. Instrumk. 15. pp. 273-278, 1895.)—The author distinguishes two classes of mercurial air-pumps—reservoir-pumps (Kolbenpumpen), of which, presumably, Geissler's may be taken as a type, and drop-pumps (Tropfenpumpen), of which Sprengel's is a typical example. Of the latter class the author uses an improved modification of an apparatus described in Zschr. Instrumk. 14. pp. 125-128, 1894, of which a short account is given in No. 17 of this year's Abstracts; of the former class he uses one described in the article under consideration. It is apparently considered that for a fair comparison the two pumps, provided by a Berlin firm, should have approximately the same money-value. The method by which the degree of rarefaction was measured is explained, and precise figures are given of the results obtained. At the commencement the reservoir-pump (capacity 800 c.cm.) works more quickly than the drop-pump—a relationship which is reversed as soon as the pressure falls below 0.1 mm. An advantage of the former over the latter is that it is not so breakable; but a disadvantage is that it requires more mercury.

A. Gs.

656. *Solar Radiation.* **A. Bartoli** and **E. Stracciati.** (N. Cim. 4. 2. pp. 5-17, 1895.)—Pyrheliometer observations made on the Giogo dello Stelvio, in the Italian Alps, at an altitude of 2850 m., during the summer and autumn of 1894, were compared with observations made on Etna at a height of 3000 m. and on the Tuscan Apennines. It was found that the quantity of solar radiation transmitted through the atmosphere at equal altitudes of the sun depends, *ceteris paribus*, chiefly upon the tension of the aqueous vapour, quite apart from the hygrometric state. Thus, on fine days with the same vapour-tension the amount of solar radiation transmitted is the same, but the amount decreases rapidly as this tension rises and the amount of vapour increases. With a perfectly clear sky the radiation transmitted is greater when the sky is dark blue than when it is light blue; hence the necessity, when comparing various heliothermic observations, of determining the colour of the sky by means of Arago's polariscyanometer or other instrument of precision. Some empirical actinometers were also compared with the pyrheliometer. The gilt and blackened sphere actinometer devised by Violle gives results depending upon the force of the wind. The difference

between the two blackened thermometers inside the two spheres tends to zero with a high wind and to a maximum during a calm. But this difference also depends upon the solar heat reflected and diffused by the ground, by surrounding objects, by the atmosphere, and by clouds. But on a perfectly clear and calm day the instrument, when placed in a locality free from snow and full of vegetation, gives very nearly correct indications. The Montsouris patterns of Arago's vacuum actinometer and the alcohol lucimeter, though less affected by wind, are subject to the same errors.

E. E. F.

657. *Brightness of the Eclipsed Moon.* **J. v. Hepperger.** (Wien. Ber. 104. 3. Part II a. pp. 189-225, 1895.)—The brightness of the surface of the moon within the shadow of the earth depends upon the refraction and absorption of the sun's rays in passing through the earth's atmosphere. The total deviation undergone by such a ray is twice the horizontal refraction at the vertex of curvature. The author calculates these horizontal refractions for various heights above the earth's surface, upon the basis of the various theories concerning the diminution of pressure at greater heights. Arguing from the incandescence of meteorites, he shows that the decrease of density as the elevation increases is not so rapid as would follow from Ivory's theory, but that Bessel's formula is more likely to be correct. The refractions and absorptions are calculated for various heights, and from these are deduced the ratios between the eclipsed and ordinary luminosities for the various portions of the shadow. One conclusion reached is that at the beginning and end of totality the element of the moon's disc furthest from the centre of shadow is 200 or 300 times as bright as the centre. As regards the apparent excess of the size of the umbra beyond the geometrical shadow, this seems to be a physiological effect due to the circumstance that the eye is incapable of detecting minute differences of brightness below a certain minimum of intensity. The value for the apparent increase of the umbra, being $\frac{1}{49}$ th of the radius, corresponds to that observed by Maedler and Schmidt.

E. E. F.

658. *Thermal Conductivity of Copper.*—Part II. *At Low Temperatures.* **R. W. Quick** and **B. S. Lanphear.** (Phys. Rev. 3. pp. 1-20, 1895.)—In addition to the range of 70° to 170° C., measurements for which were described in Part I., the thermal conductivity was determined for the range of -54° to -13°. The temperature was determined as before by the change of electrical resistance in a copper wire surrounding the bar experimented upon. Since the temperature-coefficient of this resistance is practically the same for all temperatures, the resistance was only determined for melting mercury and melting ice, and the other values were interpolated. The results of measurements of K, the thermal conductivity, show that its average value over the

cold range is slightly higher than the average value over the hot range, being in the former case 0.994, in the latter 0.954. A curious fact is the much greater slope of the curve over low temperatures, but otherwise the curves are nearly the same. From these results one of two inferences may be drawn: first, that a maximum value of K exists at a temperature near 0° , since, if the two curves of conductivity are joined, a point of inflexion occurs between -10° and $+70^\circ$; or that the observations are inaccurate, which is less probable. Over both ranges of temperature the results show an increase of K with increase of temperature. All the values of K are considerably less than those obtained by R. W. Stewart for electrolytic copper—a fact indicating that conductivity increases with the purity of the metal. For 0° , however, the values obtained by extrapolation from Stewart's and the author's curves are nearly identical.

E. E. F.

659. *Critical Temperature of Hydrogen: a Correction.*—[In connection with my abstract of Natanson's paper in the July number of this Journal, it may be desirable to point out that the critical constants of hydrogen were fully investigated by the late Wroblewski as long ago as 1889, and his results published in a paper entitled "Die Zusammendruckbarkeit des Wasserstoffes" (Wiener Sitzb. 1889). From the notice which appeared in the 'Electrical Review' for June 1895, we learn that Wroblewski's value for the critical temperature of hydrogen was -240.4°C. , the critical pressure being 13.3 atmospheres and the critical density 0.027. Natanson does not appear to have made any fresh experiments on the subject, and the conclusions arrived at in his paper are therefore not results of independent original investigation.]

G. H. B.

LIGHT.

660. *Absorption-Spectrum of Liquid Air.* **Liveing and Dewar.** (C. R. 121. pp. 162-164, 1895.)—The authors state that their experiments are the outcome of a suggestion by Cornu that it would be interesting to examine if the absorption-bands are developed as well when the density of oxygen is increased by diminution of temperature as when the gas is compressed at higher temperatures. The absorptions of a thickness of .4 cm. of liquid oxygen and 1.9 cm. of liquid air (a ray of light will pass through approximately the same quantity of oxygen in each case) were compared: the absorption-bands due to the oxygen were much more intense than those due to the air. A mixture was made by mixing liquefied air with an equal volume of liquid oxygen. According to the law of Janssen, since the mixture contains oxygen with a density about three times greater than that of the oxygen in the liquid air, the absorption of the former should be three squared, *i. e.* nine times greater than the latter. The authors' observations accord with this result; they agree also with the theory of the continuity between the liquid and gaseous states. Solid oxygen has not yet been obtained; it is doubtful whether the oxygen in liquid air exists as a solid or liquid, but so far as the absorption is concerned it behaves as if it were liquid. A. Gs.

661. *Abnormal Refraction over Water Surfaces.* **C. Dufour.** (C. R. 121. pp. 193-194, 1895.)—On the lake of Geneva abnormal refraction-phenomena are frequent. When the air is colder than the water, fine mirages are observed; when warmer, the castle of Chillon, which under ordinary conditions would be invisible even if it had double its height, can be seen at Morges. The author points out that these effects would render observations of solar and stellar altitudes faulty, and suggests the compilation of tables making the necessary corrections for different temperatures of the air and sea. H. B.

HEAT.

662. *Thermodynamic Potential.* **E. Beltrami.** (Rend. Acc. Linc. 4. pp. 473-480, 1895.)—What, in general, are the thermodynamic processes that admit a potential? The general equations are

$$dQ = dE + dL = t dF,$$

$$dL = \Sigma p dv,$$

where F denotes the entropy, L the work done, and v_1, \dots, v_n the geometric variables which with the absolute temperature t define the state of the system. If the process admits a thermodynamic potential H , then

$$p = -\partial H / \partial v,$$

and as dL is not a perfect differential, H must depend on some parameter u which is a function of t and the variables v , and must be considered constant in the deduction of the values of p .

If H then is expressed as a function of u, v_1, \dots, v_n , wherein t is contained only implicitly, we have

$$dH = (\partial H / \partial u) du - dL,$$

and thus $t dF = dE - dH + (\partial H / \partial u) du$;

so that, if $\psi \equiv H - E + tF$,

then $d\psi = F dt + (\partial H / \partial u) du$.

If u is a function of t only, then ψ must be also, and we shall have

$$F = -\partial H / \partial t + d\psi / dt.$$

If, however, u is a function of a single variable v in addition to t , then u and t are independent of each other, and thus ψ must be reducible to the form of a function of t and u ; so that

$$F = \partial \psi / \partial t, \quad \partial H / \partial u = \partial \psi / \partial u.$$

The former of these equations indicates that F is a function of u and t , and therefore that u can be expressed as a function of t and F , or

$$u = f(t, F):$$

and this is the condition that the process considered admits a potential. We also have

$$E = H + t \partial \psi / \partial t - \psi,$$

H being the *free* and $t \partial \psi / \partial t - \psi$ the *bound* energy.

In the case where $u = F^m t^n$, we have

$$\psi = m u^{1/m} t^{1-n/m} / (m-n),$$

and thus

$$H = E + ntF/(m-n) \quad \text{and} \quad \partial H/\partial u = F_{1-m} t^{1-n}/(m-n),$$

no greater generality being obtained by introducing an arbitrary function of u in the value of ψ : this reduces to an isothermal process for $m=0, n=1$, and to an isentropic process for $m=1, n=0$.

Also when $u = t\chi(F)$ or $F = \phi'(t/u)$, we have

$$\psi = u\phi(t/u);$$

whence $u dF = t dF$ if $F \equiv -\partial H/\partial u$; so that

$$dQ = dE + dL = u dF,$$

and $p = -\partial H/\partial v$, $F = -\partial H/\partial u$, $E = H - u\partial H/\partial u$.

If $K \equiv H + \Sigma p v$ is expressed as a function of u, p_1, \dots, p_n , we have similarly

$$v = \partial K/\partial p, \quad F = \partial \psi/\partial t, \quad \partial K/\partial u = \partial \psi/\partial u,$$

$$E = K - \Sigma p \partial K/\partial p + t \partial \psi/\partial t - \psi.$$

Herein putting $K_1 \equiv K - \psi$, and taking one variable v only, we obtain the usual formulæ for the so-called thermodynamic potential at constant pressure, which refers to isothermal processes. For an isentropic process we have, by the method above given,

$$v = \partial K/\partial p, \quad t = \partial K/\partial F, \quad E = K - \Sigma p \partial K/\partial p.$$

R. E. B.

663. *Characteristic Equation and Thermal Capacities of Water.*
A. Manair. (N. Cim. 4. 2. pp. 365-373, 1895.)—By the help of Clausius' tables and Battelli's experimental determination of the critical temperature and pressure of water—viz., 637°·3 C. and 194·61 atmos.—the constants of Clausius' form of characteristic

$$p/RT = (v-\alpha)^{-1} - (AT^{-n}-B)(v+\beta)^{-2}$$

are found, viz.

$$\alpha = \cdot 000842156, \quad A = 34\cdot 38, \quad B = \cdot 004475,$$

$$\beta = \cdot 001021344, \quad R = 47\cdot 05, \quad n = 1\cdot 24962;$$

and hence by Clausius' tables the specific volumes of saturated steam and water are deduced.

Writing $\phi(T) \equiv AT^{-n}-B$, we have in the usual way

$$C_v = \xi + T\phi''(T)/J(v+\beta),$$

$$C_p - C_v = \frac{T\{R(v+\beta)^2 - (v-\alpha)\phi'(T)\}^2}{J(v+\beta)\{RT(v+\beta)^3 - 2(v-\alpha)^2\phi(T)\}},$$

where ξ is the specific heat at constant volume of the vapour when

infinitely superheated. Equating further two expressions for the change of entropy, and assuming ξ to be constant, we have Morera's equation,

$$\xi \log T + \{R \log (\sigma - \alpha) + \phi'(T)/(\sigma + \beta)\}/J = \int^T (C/T) dT + \text{const.},$$

where C is the specific heat of saturated water and σ its specific volume. The mean value $\xi = .2831$ being found by combination of ten such equations with Regnault's value for C , the values of C_p , C_v were calculated: these do not agree well with those experimentally determined under, however, different physical conditions.

For the specific heat at constant pressure corresponding to ξ we obtain

$$\rho \equiv \xi + R/J = .3938,$$

which is much less than Regnault's observed value .475, and much greater than .305, the value obtained by applying the formula for perfect gases.

R. E. B.

664. *Adiabatic Expansion near the Critical Point.* **L. Natan-son.** (Zschr. phys. Chem. 17. pp. 267-276, 1895; Bull. d. l'Acad. d. Sc. de Cracovie, April 1895, pp. 130-142.)—If m is the proportion of vapour in a mixture of liquid and its vapour, the lines given by $m = \text{const.}$ may be called *isopsychrics*. Now it is known that the rate of vaporisation in such a mixture during adiabatic expansion has the same sign as $1 - m/\mu$, where μ is the ratio of the specific heat of the saturated liquid to the excess of this specific heat over that of the saturated vapour; so that expansion along an adiabatic is accompanied by vaporisation or condensation according as the adiabatic lies to the left or right of the curve given by $m = \mu$, which may be called the *neutral line*. It is obvious, then, that the isopsychric $m = c$ touches the adiabatic which passes through its intersection with the isothermal for which $\mu = c$, the point of contact lying on the neutral line. Now the specific heat of saturated liquid increases in general continuously with the temperature up to $+\infty$ at the critical point, while that of saturated vapour is negative at low temperatures, changes sign at a temperature called the *first point of inversion*, changes sign again at a temperature called the *second point of inversion* after having increased to a positive maximum, and finally diminishes to $-\infty$ at the critical point: hence μ increases at first up to a maximum value greater than 1 and then diminishes to a value at the critical point which is most probably $\frac{1}{2}$, having the value 1 at both points of inversion. The saturation-curve—i. e., the locus of the points representing saturated liquid only and saturated vapour only—is made up of the isopsychrics $m = 0$ and $m = 1$; so that the adiabatics through the points of inversion touch the saturation-curve: hence that through the second point of inversion and the neighbouring adiabatics to its right do not there enter the region of coexistence of the liquid and vapour states; so that expansion from a high

temperature along these adiabatics does not there entail condensation. But the adiabatics which cut the saturation-curve above the second point of inversion must cut it again below this point, and therefore expansion from a high temperature along them produces a momentary condensation which further expansion removes. Lastly, expansion from a high temperature along an adiabatic to the left of the *critical* adiabatic (*i. e.*, that which passes through the critical point) always results in gradual vaporisation after the saturation-curve has been reached. These conclusions account for all the phenomena observed by Olszewski in the adiabatic expansion of hydrogen near its critical point -232° .

Assuming the law of corresponding temperatures and taking, from rather uncertain data, the specific temperature of the first point of inversion to be $\cdot 75$, Natanson finds -242° for the first point of inversion in the case of hydrogen. R. E. B.

665. *Radiation through Liquids.* **C. Friedel.** (Wied. Ann. 55. pp. 453-478, 1895.)—A large number of organic liquids and a few aqueous solutions were experimented upon. They were enclosed in a glass cell between a hot box and a thermopile, and their diathermancy (transmissivity) was measured by the effect of their interposition upon the galvanometer. Whenever, under otherwise similar conditions, hydrogen, hydroxyl, oxygen, or nitrogen are replaced by sulphur or halogens, the transmissivity increases considerably. In homologous series the transmissivity changes regularly with every addition of CH_2 , but the direction of this change depends upon the nature of the other atoms contained in the molecule. The absorptive power of a compound does not essentially depend upon the size of the molecule, but appears to be characteristic of the constituents of a compound. Of the various elements investigated, hydrogen, oxygen, and nitrogen (oxygen least of the three) have the greatest influence towards increasing the absorptive power of compounds. Carbon appears to have very little influence. In isomeric compounds the transmissivity differs both with differences of atomic volume and with different linkages of the atoms amongst each other. In saturated compounds it always increases with the atomic volume. A rough sequence of increasing effect upon absorptive power is the following:—Sn, J, Br, Cl, S, C, O, H, N, carbonyl. As a means of testing the purity of organic liquids or salts which are soluble in highly transmissive liquids, the determination of their transmissivity excels all known methods in delicacy. E. E. F.

666. *Influence of Temperature on Viscosity of Benzol and Ethyl Ether above their Boiling-Points.* **A. Heydweiller.** (Wied. Ann. 55. pp. 561-576, 1895.)—The object of the experiments is to obtain some knowledge of the viscosity of liquids between their boiling and critical points. The liquid is placed in a glass tube

shaped like a very elongated O, and having one limb capillary (0.01 cm. diameter); some mercury is also inserted in the tube, which is then exhausted and sealed, so that it contains only mercury, liquid and vapour of liquid. It is then heated in a glycerine bath to the desired temperature, the tube is tilted so that the liquid occupies the part just below the capillary portion, and on bringing the tube to the vertical position again the pressure of the mercury drives the liquid through the capillary portion. The time of flow between two marks, and the temperature, are noted, and the viscosity is deduced from these observations. Stoel, who has previously experimented on methyl chloride, finds that the viscosity (η) is related to the absolute temperature (θ) by an expression of the form

$$\eta = ae^{-b\theta},$$

so that $\log \eta$ is a linear function of the temperature. At low temperatures, however, the curve of $\log \eta$ and θ is convex to the temperature-axis, at high temperatures concave, while the intermediate portion is a straight line. The author's results agree with this; and he finds that the constant b has nearly the same value for methyl chloride, ether, and benzol, so that at corresponding temperatures all these substances have the same viscosity. At a temperature 0.865 times the critical temperature the viscosity is about 10^{-3} absolute c.g.s. units.

J. L. H.

667. *Kinetic Energy of Heat-Currents and the corresponding Dissipation-Function.* **L. Natanson.** (Zschr. phys. Chem. 16. pp. 289-302, 1895.)—Consider a fluid medium, of density ρ , composed of numerous molecules in motion. Let u, v, w be the velocity-components of the mass-centre of a volume-element $dx dy dz$, and let the velocity-components of one of the molecules in the element be $u+\xi, v+\eta, w+\zeta$. Then, if Q denote any function of $u+\xi, v+\eta, w+\zeta$, and if square brackets denote mean values taken over the element, it has been proved by the author in a previous paper* that

$$\begin{aligned} \rho \frac{d[Q]}{dt} + \frac{\partial}{\partial x} ([\xi Q] \rho) + \frac{\partial}{\partial y} ([\eta Q] \rho) + \frac{\partial}{\partial z} ([\zeta Q] \rho) \\ = \rho \left(\frac{\delta[Q]}{\delta t} + X \frac{\partial[Q]}{\partial u} + Y \frac{\partial[Q]}{\partial v} + Z \frac{\partial[Q]}{\partial w} \right), \quad (1) \end{aligned}$$

where X, Y, Z are the components of the accelerative effect of external forces at the point (x, y, z) , and $\delta/\delta t$ refers to changes produced by encounters or mutual actions of the molecules. By giving particular forms to Q , Natanson now deduces equations representing the diffusion of heat through the medium. After

* Zschr. phys. Chem. 13. p. 437.

numerous mathematical substitutions and transformations, he arrives at the following result :

$$\text{if } A = \frac{1}{4}\rho[(\xi^2 + \eta^2 + \zeta^2)^2];$$

then

$$\begin{aligned} \frac{\partial}{\partial t} \iiint A \, dx \, dy \, dz = & - \iint A (lu + mv + nw) \, dS \\ & + \frac{5}{3} \iiint ([\xi^2] + [\eta^2] + [\zeta^2]) F \, dx \, dy \, dz \\ & - \frac{5}{3} \iiint p ([\xi^2] + [\eta^2] + [\zeta^2]) \left(\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) dx \, dy \, dz \\ & - \frac{5}{6} \iint \rho ([\xi^2] + [\eta^2] + [\zeta^2]) (lr_x + mr_y + nr_z) \, dS \\ & + \frac{5}{6} \iiint \left(\rho r_x \frac{\partial}{\partial x} + \rho r_y \frac{\partial}{\partial y} + \rho r_z \frac{\partial}{\partial z} \right) ([\xi^2] + [\eta^2] + [\zeta^2]) \, dx \, dy \, dz \dots, \quad (2) \end{aligned}$$

where

$$r_x = [\xi(\xi^2 + \eta^2 + \zeta^2)],$$

p is the hydrostatic pressure, and F denotes Lord Rayleigh's dissipation-function, *i. e.*

$$F = (\rho - \rho[\xi^2]) \frac{\partial u}{\partial x} + \dots + \dots - \rho[\eta\zeta] \left(\frac{\partial v}{\partial z} + \frac{\partial w}{\partial y} \right) - \dots - \dots$$

Now the integral $\iiint A \, dx \, dy \, dz$ stands in the same relation to the motion of heat in the medium as the kinetic energy of a fluid to the motion of the fluid; and for this reason the integral may be called *the kinetic energy of the heat-currents* in the medium—a convention closely analogous with that made by Maxwell in the case of electric currents. Equation (2) shows that the rate of change of this quantity is made up of five terms, of which the first is due to the flow of matter across the bounding-surface S , the second to the conversion of energy into heat in consequence of viscosity, the third to the heat produced by compression of the medium itself, and the fourth to the flow of heat across the bounding-surface S . The fifth term Natanson reduces to the form

$$\frac{1}{4} \iiint \left\{ \frac{1}{\rho[\xi^2]} \frac{\delta}{\delta t} (\rho^2 r_x^2) + \dots + \dots \right\} dx \, dy \, dz;$$

and this represents the rate of change of the volume-integral of A due to intermolecular action. If this be negative, the diffusion of heat throughout the medium will gradually subside, as we know from experience that it actually does; if the inter-

molecular action were such as to make this integral positive, we should have a medium in which the heat-currents increased without limit, and although this is contrary to experience the dynamical theory is not inconsistent with the existence of such a medium. The author then proceeds to deduce the equations of conduction of heat in the medium. The present theory is not based on any particular law of intermolecular force; but it is important to observe that in the course of the mathematical work certain terms have been neglected, so that the results are at best only approximate. Whether the present theory is applicable to liquids as well as gases, or whether the neglected terms become important in the case of media whose molecules are densely crowded together, is a question which might well be examined more fully. G. H. B.

668. *Temperature of Metal Bars.* **H. Stadthagen.** (Zschr. Instrumk. 15. pp. 280-282, 1895.)—Throughout the operation of comparing the lengths of two metal bars, it is generally possible so to control matters that no great error results from assuming the two to have the same temperature. The author discusses the correction to be applied in the extreme case, when a mean temperature between the bar and the standard is adopted. Neglecting squares and higher powers of the temperature-coefficients, the correction is shown to be equal to the product of the difference of temperature of the two rods, and the mean of the two coefficients. The correction is thus a function of the *sum*, and not of the *difference*, of the coefficients. R. A.

669. *Melting- and Boiling-Points.* **H. Le Chatelier.** (C. R. 121. pp. 323-326, 1895.)—Since the general adoption of thermoelectric pyrometers, graduated by Violle's method, the determinations of the melting-points of iron, steel, etc. have given results differing by not more than 10° on the whole. It does not follow, however, that these melting-points are really correct. Recent determinations of the melting-point of gold, for instance, have generally given higher values than Violle's: from specific heat of platinum, Violle 1045° ; thermoelectric couples graduated with help of air-thermometer, Barus 1095° , Holborn and Wien 1072° ; electric resistance of platinum, extrapolation above 450° , Callendar 1035° , Heycock and Neville 1062° . Direct measurements with air-thermometers have not been made. Le Chatelier graduates the couple with the help of the boiling-point of zinc, which Violle directly, and Barus and Becquerel indirectly, fix at 930° . To protect the couple against the zinc vapour, he covers the wires with crossed asbestos fibre, and fits them into a glass tube closed at one end. The melting glass forms a varnish which is impermeable to the zinc, at any rate for the few minutes of an experiment. The author adopts for his measurements the photo-

graphic method of which he availed himself for his researches on clay, and finds that gold melts at 1050° or 1060° . If the former is accepted, the melting-points of selenium and cadmium would be 688° and 770° ; Carnelley found 680° and 768° . The melting-point of silver the author determined in an oxidising atmosphere, as a reducing medium affects the point; silver melts 100° or 104° lower than gold. The conclusion is that the melting-point of gold lies above probably 1045° , but certainly not more than 20° ; for the present it will be best to adhere to 1045° .

H. B.

ELECTRICITY.

670. *Comparison between Electric Motors for Continuous Currents and Motors for Polyphasic Currents.* **Duez.** (C. R. 121. pp. 160–162, 1895.)—The paper is mathematical, contains a comparison and simple demonstration of the formulæ involved when the turning-moments are determined, and a comparison of the action of the two motors when used in the transmission of force. A. Gs.

671. *Electric Discharges of the Torpedo.* **D'Arsonval.** (C. R. 121. pp. 145–151, 1895.)—The author is confirmed in his view that muscular contractions and electric discharges are intimately connected, and that the muscle and the electric organ obey the same laws. He observed with the help of a Deprez-d'Arsonval galvanograph, consisting of a current-coil wound on an aluminium bobbin suspended in a strong magnetic field and attached to the rubber membrane of an air-drum, communicating by means of a rubber tube with a smaller drum; the instrument is very aperiodic. He further used a Cardew voltmeter, a silver wire 0.1 mm. thick, 40 cm. long, held by binding-screws, and stretched by another wire attached to a rubber spring. The torpedo is placed on a metal plate covered by 1 cm. of water. Tinfoil electrodes, joined by a strip of tinfoil, are applied to the back: the tinfoil forms the positive electrode, the metal the negative. The animal is slightly pinched. Six or ten discharges, of a duration of 0.05 or 0.1 sec., follow one another at intervals of 0.01 sec.; the third is generally the strongest; the direction does not vary. Torpedos of 25 and 35 cm. diameter gave currents of from 8 to 17 volts and 1 to 7 amperes, strong enough to destroy one 4-volt and 1-ampere incandescence lamp, and to light three such in series. Geissler tubes can also be worked. The two organs function simultaneously, and are exhausted after four or five discharges. If the organ of one side only is discharged, and a lamp applied to the other side, the lamp burns brightly, which proves that the exhaustion takes place in the electric organ and not in the nerve. The temperature of the organ rises by 0.2 or 0.3 during the discharge. If the nerve is cut and then irritated, the same but weaker phenomena take place. A stethoscope reveals that about 100 vibrations occur per second. The anterior portion of the electric organ seems to function quicker than the posterior part. No difference of potential exists in the state of rest.—Marey accentuated the analogy and identity of phase of muscular and electrical effects.

H. B.

672. *Capillary Electric Phenomena.* **H. Luggin.** (Zschr. phys. Chem. 16. pp. 677–707, 1895.)—The curve indicating the superficial tension of mercury in dilute sulphuric acid rises to

a maximum, and then descends when the polarising E.M.F. is continuously increased. Up to the present, experiments have been confined to mercury and dilute amalgams in contact with either dilute acids or aqueous solutions of salts. The author extends the observations to other liquid metals in contact with fused saline electrolytes. In the first experiments a mixture of LiBr and KBr is the electrolyte, and lead is the metal. The U-tube containing the metal and electrolyte is arranged in a small oven fitted with windows. If the polarising E.M.F. be gradually increased, the superficial tension rises rapidly at first, but afterwards more slowly. Other experiments with melted zinc chloride and an easily fusible mixture of KNO_3 and NaNO_3 give similar results.

A second section of the paper deals with the determination of the value of the potential difference required to produce the maximum superficial tension of mercury in contact with a number of different aqueous electrolytes. The results cannot be accounted for by Helmholtz' theory of a double layer of electricity. S. S.

673. *Axial Character of Lines of Magnetic Force: a Conclusion from the Existence of the Hall-Effect.* **F. Koláček.** (Wied. Ann. 55. pp. 503-506, 1895.)—Various considerations are adduced to show that although the equations of the electric field are a reciprocal system—that is to say, in an insulating medium a reciprocal relation connects the electric and the magnetic forces—there is an essential difference between the two forces. For one thing, a strong electric field may result in an electric spark: no *magnetic spark* has yet been obtained with the strongest fields yet tried. Also, new theories proceed from the point of view that the magnetic phenomena depend on cyclic motions round the so-called lines of magnetic force as axes. Thus we have Ampère's explanation of magnetism by molecular currents, and Lord Kelvin's conclusion that magneto-optic rotation is due to a component of angular momentum having its axis parallel to the direction of the magnetic force, and due to the rotation of molecules of or in the medium. Thus the direction of the magnetic force is that of an axis of cyclic motion. Calling a vector a "direction" when some phenomenon has place along it, and an "axis" when some phenomenon has place round it, the author deduces from the Hall phenomenon that the magnetic force must be essentially an axis. Referring to the Hall-effect, calling J the primary current along the gold-leaf, i the "Hall-current" through the galvanometer applied at two points on the two edges of the leaf, he argues that if (A) the primary current, the Hall-current, and the magnetic force be all "directions," or (B) if the two currents be "axes" and a line of force a "direction," there is nothing to determine which of two directions in the plate the Hall-effect should have; and (C) that if the current possesses both the qualities of "direction" and "axis," while the magnetic force is a "direction," there

can be no reversal of the Hall-effect with reversal of the magnetic force, which contradicts experiment. The author finds these difficulties removed when the magnetic force is regarded as an "axis." He states also that the Hall-effect does not furnish an answer to the question as to whether the lines of magnetic force are the axes of a static cyclic polarisation, or a cyclic phenomenon in some way depending upon the time. A. GY.

674. *Electrification produced by the Evaporation of Volatile Conducting Liquids.* **P. Pettinelli.** (N. Cim. 4. 2. pp. 36-38, 1895.)—The author has continued the investigations of Bartoli, using volatile liquids—such as ethyl alcohol, ether, acetone, allyl aldehyde, propyl aldehyde—rendered conducting by containing a small quantity of dissolved bromine or water. In no case were signs of electrification due to evaporation obtained. W. W.

675. *Electric Lighting by Incandescence.* **A. Witz.** (C. R. 121. pp. 306-308, 1895.)—The object of the research is to determine the efficiency of lighting by means of incandescent gases. The gases are rendered incandescent by means of either an induction-coil or a Holtz machine. In the first case the watts consumed in the tube can be determined, and in the second case the power consumed is taken to be the difference of the powers required to drive the Holtz machine at a given speed with and without the tube. The author finds that the efficiency of lighting by this method is much less than by the ordinary incandescent lamp with carbon filament. W. G. R.

676. *Side Flashes from Electrical Conductors.* **A. Broca.** (Bull. Soc. Franç. Phys. 67. 1895.)—The author studies the phenomenon of side flashes by using vacuum-tubes excited unipolarly. An induction-coil is used as the exciting machine. When a sufficiently disruptive spark passes the vacuum-tubes become illuminated, but if the spark becomes an arc the illumination disappears; the illumination reappears if the arc is blown, or if a piece of cardboard is interposed the tubes become illuminated whenever the cardboard is pierced. The conclusion is that whenever a spark occurs at any point of a circuit, the side flashes given by the circuit are longest when the circuit is closed. W. G. R.

677. *Experiments with Alternate-Current Arcs.* **A. Blondel.** (L'Ind. El. 4. pp. 329-330, 1895.)—Some writers assert that the small value of the power-factor in the case of an alternate-current arc is due to a difference of phase between the current and the difference of potential between the carbons. The author of the paper denies this, and says that the cause is to be found in the fact that the current is almost zero for an appreciable fraction of the period of an alternation. On examining actual curves taken

by his photographic stroboscopic method, the author finds that there is a slight lag of the current behind the potential-difference. He observes that this lag of the current cannot be explained by supposing an electromotive force of polarisation in the arc, because this would cause the current to lead; he then hazards the supposition that it may be due to the presence of a thermoelectric electromotive force in the same sense as the current, and being produced at the point of contact of the arc and the positive carbon when at the temperature of volatilisation, and disappearing when the temperature is sufficiently low. W. G. R.

678. *Galvanic Polarisation of Nickel, Cobalt, and Iron.* **E. Vogel.** (Wied. Ann. 55. pp. 610-622, 1895.)—The measurements are made by the method of Fuchs, which allows the E.M.F. of polarisation to be measured without interrupting the exciting current. Nickel plates used as electrodes in a nickel-sulphate solution give a polarisation which rapidly increases with the strength of the current to a maximum value at the anode of 1.96 volts, and at the kathode of 1.46 volts. This maximum remains practically constant when the current is increased from 0.84 to 4 amperes. The higher value at the anode is attributed to the formation of an electro-negative layer of oxide. The kathode becomes covered with a black flocculent layer under which the nickel deposits as a bright adherent coating, some gas being evolved at the same time. The concentration of the NiSO_4 solution makes little difference in the result. The addition of ammonium salts to the nickel-sulphate solution diminishes the polarisation. In 5 per cent. sulphuric acid the maximum E.M.F. of polarisation is, at the kathode 1.22, at the anode 1.07 volts. 2 per cent. sulphuric acid gives smaller values. Cobalt plates in cobalt-sulphate solution give a polarisation increasing slowly with the strength of the current to a maximum of 1.36 volts at the kathode, and of 1.14 volts at the anode. The phenomena observed during the electrolysis are similar to those noticed with nickel. With cobalt in 5 per cent. sulphuric acid, a maximum polarisation of 0.99 volt at the anode and 0.84 volt at the kathode is obtained. Pure iron in ferrous sulphate solution gives no constant results until the current has passed for some time. The maximum polarisation then obtained is 0.37 volt at the anode and 0.27 at the kathode. With 5 per cent. sulphuric acid in place of the ferrous sulphate, almost exactly the same numbers are obtained. The addition of ammonium chloride to the FeSO_4 solution diminishes the polarisation. T. E.

679. *Conductivity of Solutions of Salts in Acetone.* **S. v. Laszczyński.** (Zschr. Electrochemie, 4. pp. 55-57, 1895.)—Although solutions in acetone have a very high resistance, the author has determined the constants for the following salts in that solvent:—KI, LiCl, KCNS, NaCNS, NH_4CNS , HgCl_2 , and HgNO_3 . The values for μ_∞ in the case of KI in the following solvents are:—ethyl alcohol

46.1, water 121.6, acetone 160. He points out that these numbers are nearly inversely as the values for the viscosities of the different solvents examined, as might be expected from theory. The same solutions were also electrolysed. S. R.

680. *Electrical Vibrations in Tesla's Experiments.* **A. Oberbeck.** (Wied. Ann. 55. pp. 623-632, 1895.)—The author considers mathematically the electrical conditions which obtain when a charged condenser is allowed to discharge itself through an induction-coil in the neighbourhood of a secondary circuit consisting of a condenser and induction-coil. He first forms the equations of motion, and then assuming that the charge in the first condenser is proportional to $e^{\lambda t}$, where λ is complex, obtains an equation of the fourth degree for λ . This he is unable to solve; but by neglecting the resistances of both circuits he reduces the equation to a quadratic in λ^2 . This indicates the existence of an undamped electrical vibration in each circuit compounded of two vibrations of different periods. If T, T' are the times of vibration of these oscillations, and T_1, T_2 are the times of vibration of the separate circuits, then $T^2 > \frac{1}{2}(T_1^2 + T_2^2) > T'^2$. With this same approximation he determines the amplitudes of the two components for the two circuits. By supposing that the damping coefficient α is small compared with β , when $-\alpha + i\beta = \lambda$, the rates of decay of the two components are obtained. A numerical example concludes the paper. G. F. C. S.

681. *General Solution of Maxwell's Equations for a Homogeneous Conducting Dielectric.* **Birkeland.** (C. R. 120. pp. 1046-1049, 1895.)—An abstract of a paper to appear in the 'Archives de Genève.' The state of the electromagnetic field being supposed known at every point at the time $t=0$, the author obtains (very complicated) expressions for the electric and magnetic forces at any point at any subsequent epoch. The velocity of propagation of disturbances appears to depend only upon the specific inductive capacity and the magnetic permeability of the medium, and not upon the conductivity. G. F. C. S.

682. *Effect of Dissolved Gases upon the Silver Voltmeter.* **J. E. Myers.** (Wied. Ann. 55. pp. 288-296, 1895.)—The author investigates the effect of oxygen, nitrogen, and CO_2 upon the amount of silver deposited from a neutral AgNO_3 solution by a given current. He finds (in agreement with Schuster and Crossley, Proc. R. S. 50. p. 344, 1892) that in 20-40 per cent. solutions about .1 per cent. less silver is deposited when the voltmeter is in air than when it is in "vacuum" (1.5 cm. Hg). For a 5 per cent. solution the differences are smaller but irregular. When the solution is saturated with oxygen the deposit is .055 per cent. less than when the solution is saturated with air. On

the contrary, a solution saturated with nitrogen gives a deposit .05 per cent. greater than when saturated with air. Schuster and Crossley found that when the solution is saturated with oxygen the deposits are .04 per cent. less than when the solution is saturated with air. The author finds that when the solution is saturated with CO_2 , the deposit is .055 per cent. less than when the solution is saturated with air. He also attempted to find the effect of hydrogen, but found that all the "hydrogen" he could make had a reducing action upon the AgNO_3 solution. He finds that the specific resistance of a 5 per cent. solution is appreciably the same whether it was saturated with air or was air-free. He also noticed that under a pressure of 1.6 cm. Hg there is a vigorous development of gas at the anode, when the current reached .25 ampere. He finds that the black deposit upon the anode is practically all silver oxide Ag_2O_2 , but does not state what ratio the amount of this Ag_2O_2 bears to the amount of silver deposited upon the kathode. [It would have been interesting to know the effect of gradual increase of pressure in the case of the various gases. The author only considers the pressures 76 cm. and 1-2 cm.]

G. F. C. S.

683. *Vibrations of a Non-Simple Hertzian Oscillator.* **J. v. Geitler.** (Wied. Ann. 55. pp. 513-524, 1895.)—The object in view was to obtain an oscillator really possessing more than one period, as distinguished from so-called Multiple Resonance attributable to a single damped oscillation. The form of oscillator used had two pairs of plates forming two distinct air-condensers. These condensers stood in line in one plane, and were on either side connected by wires which also were prolonged beyond one of the condensers so as to terminate in discharging knobs. Either pair of plates could be removed at will, so as to leave a single Hertzian oscillator of a definite period of the Blondlot type. The resonance and circuit consisted of two parallel wires which ran parallel to the wires of the oscillator. These at one end were connected to the plates of a special form of electrometer of small capacity. A bridging wire slid along and varied the length of the resonating circuit as required for resonance. First the position of the bridge was ascertained with each condenser removed in turn. Then with both in use. This was done with variations in the capacity of the condensers effected by various sized plates, as well as by altering their distance apart. In every case when both condensers were in, oscillations of two distinct periods were found to simultaneously take place. One of these was found to be always longer, whilst the other was shorter than either of the independent periods, as ascertained by removal of each condenser. The amplitudes of these two simultaneous oscillations, as ascertained by the swing of the electrometer, were found to preserve a constant ratio for a given oscillator. By comparison of the behaviour of the various sized oscillators, such as varying the capacities of the condensers, it was found that the ratio of the amplitudes is a periodic

function of the ratio of the long and short periods. In the concluding part of the paper it is shown how these observations are in accordance with theoretical considerations. F. L. T.

684. *Galvanometer for Photographing Alternating Current-Curves.* **H. J. Hotchkiss** and **F. E. Millis.** (Phys. Rev. 3. pp. 49-62, 1895.)—The galvanometer described was made for use in an experimental study of the extra currents produced on closing a circuit containing self-induction. The spot of light from the mirror of the galvanometer is photographed on a moving plate after reflection from a modified form of Blondel's oscillograph. The galvanometer-needle is made of soft iron, and is placed in a very strong magnetic field produced between the poles of an electromagnet. In order to make the effects of inertia inappreciable, the needle and mirror are made as small as possible. The natural period of the needle is made much smaller than that of the current, so as not to affect the shape of the current-curve. The needle has a periodic time of about $\frac{1}{3500}$ second. The current under investigation passes through a coil surrounding the needle. The periodic time of the needle is obtained optically by comparison with a tuning-fork of known vibration number. Particulars of one of the galvanometers are as follows:—

Fibre	{	Material ..	Quartz.	
		Length....	14	mm.
		Diameter ..	0.14	„
Needle	{	Length....	2.4	„
		Width	1.25	„
		Thickness..	0.33	„
Mirror	{	Length....	2.00	„
		Width	1.25	„
		Thickness..	0.30	„
Approximate vibration-		} 3580		
frequency with about				
10 amperes in field				
coils.....				

The paper contains wave-forms of several generators as recorded by the galvanometer. W. G. R.

685. *Electric Resonance.* **V. Bjerknes.** (Wied. Ann. 55. pp. 121-169, 1895.)—This valuable paper is chiefly theoretical, the only experimental part being illustrative references to results previously published by the author. The object of the paper is to establish methods for experimentally determining the constants of a Hertzian oscillator and resonator by utilising the phenomenon of resonance. The course of the electrical disturbances which occur in a resonator obviously depends upon a series of parameters. If we knew these parameters we should then be able to express, as a

function of the time, the electric condition of the resonator, *e. g.*, the potential-difference of its poles, the quantity of electricity on its plates, or the current in its conducting wires. The resonance experiments are to be carried out by retaining constant the period of one of the circuits, while the period of the other is adjusted from time to time. This circuit (which may be either the oscillator or the resonator) must be calibrated so that on each occasion of its use its period during that section of the experiment is always a known quantity. The other quantities which are now chosen as the parameters to be determined are the following four, *viz.*:—the period of the unchanged circuit, the logarithmic decrement of the oscillator, the logarithmic decrement of the resonator, and finally a constant which measures the intensity of the oscillations. The theory of the behaviour of the resonator under the action of the oscillator is based upon the following differential equation:—

$$\left. \begin{aligned} \frac{d^2\phi}{dt^2} + 2\beta\frac{d\phi}{dt} + (b^2 + \beta^2)\phi &= Ae^{-at} \sin(at + a') \\ \text{with the initial conditions,} \\ t=0, \quad \phi=0, \quad \text{and} \quad \frac{d\phi}{dt}=0, \end{aligned} \right\}, \dots (1)$$

where ϕ denotes the potential-difference of the two poles of the resonator. The solution of this equation is first written

$$\phi = e^{-at}(A_1 \sin at + A_2 \cos at) + e^{-\beta t}(B_1 \sin bt + B_2 \cos bt), \quad (2)$$

in which the first term on the right expresses the “forced” vibrations whose period and damping are those of the oscillator, and the second term on the right represents the free oscillations whose period and damping are those peculiar to the resonator itself. From this form of the solution the significations of the various symbols are readily inferred. The solution is afterwards, for convenience, thrown into the form

$$\phi = M \sin(mt + m'), \quad (3)$$

in which both the amplitude M and the epoch m' are functions of the time. The value of M is next obtained, the typical cases discussed, and their peculiarities graphically exhibited. Now if an electrometer with an uncharged needle be used to measure the electrical disturbances in the resonator, its throw, y , will be proportional to

$$I = \int_0^\infty \phi^2 dt. \quad (4)$$

The relation between the electrometer throw, y , and the period, x , of the variable circuit is then obtained analytically and plotted as a curve called the *Resonance Curve*, which is fundamental in what follows. The chief feature of this curve is a well-defined maximum near to, but *not necessarily coincident with*, the place of the exact resonance. It also possesses the property that the locus of the middle points of chords parallel to the x -axis is an equilateral

hyperbola. Other properties of the resonance curve are developed and discussed, and the proposed method of utilising them explained. The entire series of experimental and mathematical operations to be performed in making a complete determination of the parameters sought may be thus summarised:—(1) The adjustable conductor is first calibrated. (2) The electrometer-throws in the resonator are read with different values of the period of the adjustable conductor [which may be either the resonator itself or the oscillator]. (3) The resonance curve is then plotted with periods as abscissæ and electrometer-throws as ordinates. From this curve and the afore-mentioned analysis we ascertain the period, X , of the invariable circuit, the corresponding electrometer throw, Y , and the mean value, ω , of the logarithmic decrement of the two conductors. (4) The experiment is then to be repeated, but with the conducting wire of one of the circuits replaced by another wire of the same dimensions, but of a different metal, so as to materially change its electrical resistance, and, in consequence, the logarithmic decrement of the circuit in question. The new resonance-curve obtained after this change yields approximately the same value of X , but new values of Y and ω . From these and the foregoing data are derived the two logarithmic decrements sought. (5) The intensity factor, A , can also be determined if the absolute constant of the electrometer is known.

E. H. B.

CHEMICAL PHYSICS.

686. *Phosphorescence of Rarefied Nitrogen after the Passage of an Electric Discharge.* **G. Séguy.** (C. R. 121. pp. 198-199, 1895.)—Nitrogen in the presence of a metallic bichloride—stannic chloride, for example—phosphoresces like oxygen after an electric discharge. The light emitted during the discharge is pink; the phosphorescence is milky white, of greatest intensity immediately after the break of the current, and gradually diminishes until it disappears at the end of from 10 to 80 seconds. A. Gs.

687. *Chemical Precipitation in Gelatinous Media.* **N. Pringsheim,** edited by E. PRINGSHEIM. (Zschr. phys. Chem. 17. pp. 473-504, 1895.)—A graduated glass tube is stopped by a plug of jelly containing 5 per cent. of gelatine. The reagents which are to act on one another are allowed to diffuse into this stopper of jelly from either end, and the position of the first formation of a precipitate and its growth is observed on the graduations. The strength of the solutions is also varied, and the influence of this factor on the growth of the precipitate is traced. The conclusions are:—(1) The growth of the precipitate is always on one side; it is either limited or unlimited, and the new layers of the precipitate add themselves on in the front. (2) The diffusion-current flows from the side of greater molecular concentration to that of less. As an example, the following may be quoted:—

Molecular Proportion.	Direction of Growth.		The Growth is:—
	KCl	AgNO ₃ .	
KCl : AgNO ₃ .			
0.25 1	←		Unlimited.
1 1		Limited.
2 1	→		Unlimited.

S. S.

688. *Solutions.* **L. de Boisbaudran.** (C. R. 120. pp. 1190-1192, 1895.)—In determining the volume of salts in aqueous solutions the author has compared the results obtained by a dilatometer with those obtained by a specific-gravity flask, and shows how the two methods may be used to mutually control each other. S. R.

689. *Electrochemical Experiments.* **R. Zsigmondy.** (Electrochemische Zschr. 2. pp. 55-58, 1895.)—The author describes some electrochemical experiments on metal deposition from their

salts which are suitable for lecture illustrations. He describes the conditions for obtaining the well known "trees," and several modifications of the earlier forms of these experiments suitable for use before large audiences. S. R.

690. *Aluminium Utensils*. **Balland**. (C. R. 121. pp. 381-383, 1895.)—The aluminium utensils now in use in the French army vary in weight, although they are made simply by stamping without any other soldering but to fix the handles. The bottles weigh from 55 to 60 gr., the flasks 160 to 169 gr., the mess tins 255 to 269 gr., the larger size 527 to 561 gr. The differences are produced by the treatment with soda, which renders the surface dim, and when a stronger bath is used blackish. The utensils wear very little, can be heated over gas and coal, and are not attacked by the food and wine, etc., as the food does not remain long in the vessels. Flasks in which ordinary water is kept for months show whitish spots near specks of impurities—iron, silicon, carbon, and on the soldered portions if other metals have been admixed. Strips of aluminium-foil, kept for four years in seine water in stoppered bottles, became covered with a coating which rubbing with powdered bricks did not remove, but which dissolved in 0.01 sulphuric acid; in some parts the corrosion had almost destroyed the foil, but the loss amounted to 3 per cent. only. In salt water the corrosion proceeds quicker, particularly where the metal is exposed to air and water; the metal becomes black, and remains so when rubbed with sand, and the handles come off; sulphuric acid restores the original brightness. The impurities are again of influence: vinegar kept in aluminium flasks indicated the level of the liquid on the outside by a whitish ring of alumina. As the old vessels contain often 8 per cent. of impurities, whilst aluminium of 99 per cent. can now be obtained, the application of aluminium will increase, but the soda-lye should be abolished as the soda does not penetrate uniformly, and a suitable aluminium solder should not contain other metals. The sanitary aspect is not touched upon. H. B.

691. *Physico-chemical Measurements*. **W. Ostwald**. (Zschr. phys. Chem. 17. pp. 427-445, 1895.)—The author reviews the recent work in physico-chemical problems, and indicates the scope which present methods are fitted for, and the general results which such investigations produce. S. R.

692. *Exact Formulæ for Osmotic Pressure etc.* **J. J. van Laar**. (Zschr. phys. Chem. 15. pp. 457-497, 1894.)—Theoretical investigations of the properties of solutions are usually limited to the case of extreme dilution, but the general case too admits of simple expression in terms of thermodynamic potential.

If p , τ denote the pressure and absolute temperature, and

V , E , H the total volume, energy, and entropy of a solution made up of n_1, n_2, \dots gram-molecules of different bodies whose concentrations are c_1, c_2, \dots , where $c \equiv n/\Sigma n$, we have

$$Z = -\tau H + E + pV$$

for the total thermodynamic potential with constant τ and p , and we may write

$$H \equiv H' - R\Sigma . n \log c,$$

where H' is independent of the concentrations in the limiting cases of a perfect gas and of an indefinitely dilute solution.

Writing

$$\Psi \equiv -Z/\tau, \quad \psi_r \equiv \partial \Psi / \partial n_r, \quad \Psi' \equiv \Psi + R\Sigma . n \log c, \quad \psi_r' \equiv \partial \Psi' / \partial n_r,$$

we have

$$\psi = \psi' - R \log c,$$

so that the properties of extremely dilute solutions are obtained by substitution of $-R \log c$ for ψ in the formulæ found for the general case.

I. General fundamental formulæ being written down, the case is considered of a single binary body of which ν gm.-mols. are dissolved in n_1 gm.-mols. of a solvent, and it is shown that, if $\sigma \equiv \nu/(n_1 + \nu)$ denotes the undissociated concentration of this body and α the actually resulting degree of dissociation (*i. e.* $\alpha\nu$ gm.-mols. of each ion being dissociated),

$$\sigma d\psi_2/d\sigma = -(1-\sigma) d\psi_1/d\sigma$$

when p and τ are constant, the subscripts 1, 2 referring respectively to the solvent and the undissociated part of the body. [This is equivalent to

$$x d\psi_2/dx = -d\psi_1/dx,$$

where $x \equiv \sigma/(1-\sigma) \equiv \nu/n_1$.]

II. It is next shown that, if ν_1, ν_2, \dots are the integral coefficients in the formula of any reaction,

$$\Sigma (\nu \partial \psi / \partial p) = -U/\tau, \quad \Sigma (\nu \partial \psi / \partial \tau) = Q/\tau^2,$$

where U and Q denote the total change of volume and the heat required for the reaction per gram-equivalent of the system.

III. The osmotic pressure from a solution towards the separated solvent is then shown to be positive and to increase with the concentration and, on the assumption of the incompressibility of the solvent under the pressures in question, to be given by

$$\pi v_l = \tau(\psi_1 - \psi_l) = R\tau(f - \log c_1),$$

where v_l and ψ_l are the volume and potential per gram-molecule of the pure liquid solvent, while the subscript 1 refers to the solvent in the solution, and $f \equiv \{\psi_1'(c_2, c_3, \dots) - \psi_1'(0)\}/R$ is a function

of the concentrations of the solutes which vanishes for extreme dilution. Thus for very dilute solutions

$$\pi v_l = -R\tau \log c_1 \simeq R\tau(1 - n_1/\Sigma n),$$

which is van't Hoff's law; for less dilute solutions of a single binary solute we have, as in I.,

$$c_1 \equiv (1 - \sigma)/(1 + \alpha\sigma)$$

and

$$-\log c_1 \simeq \sigma(1 + \alpha)\{1 + \frac{1}{2}\sigma(1 - \alpha) + \dots\} = [z - \frac{1}{2}z^2 + \dots, \text{ where } z \equiv \alpha(1 + \alpha)].$$

If the osmotic pressure would support a column of height h of the pure solvent whose molecular weight is m , then

$$\pi = gh m / v_l;$$

and thus, if $\zeta \equiv \partial Z / \partial n$,

$$\zeta_l - \zeta_1 = mgh.$$

IV. If solid salt is put into contact with a solution of itself, there will be solution, equilibrium, or precipitation according as

$$\psi_2 - \psi_b \begin{matrix} \geq \\ \leq \end{matrix} 0,$$

these symbols denoting the potential of the undissociated salt in solution and of the undissolved salt respectively per gm.-mol.; and it is shown that, if s is the value of σ and U_s , L_s the volume-change and heat of solution per gm.-mol. for saturation,

$$\tau(\partial s / \partial p) / U_s = -\tau^2(\partial s / \partial \tau) / L_s = 1 / (d\psi_2 / ds):$$

hence, since $d\psi_2 / ds$ is always negative, the concentration corresponding to saturation increases or diminishes (1) with rise of pressure according as contraction or expansion accompanies the solution and partial dissociation, (2) with rise of temperature according as heat is absorbed or emitted during the same process. These results give Clapeyron's equation,

$$d\tau / dp = \tau U_s / L_s,$$

which shows that for the solution to remain saturated and of unchanged concentration the changes of τ and p must have the same sign if U_s / L_s is positive.

For a dilute solution,

$$d\psi_2 / ds = -2R/s(2 - \alpha + \alpha s).$$

V. If the solid form of the solvent is put into contact with a solution it will melt, remain in equilibrium, or cause partial freezing-out of pure solvent from the solution according as

$$\psi_1 - \psi_a \begin{matrix} \geq \\ \leq \end{matrix} 0,$$

these symbols referring to the solvent in the solution and in the solid form respectively. Then, as in IV., if s' is the value of σ for equilibrium, $U'_{s'}$ the volume-change, and $L'_{s'}$ the latent heat of fusion accompanied by increase of dissociation per gm.-mol.,

$$\tau(\partial s'/\partial p)/U'_{s'} = -\tau^2(\partial s'/\partial \tau)/L'_{s'} = 1/(d\psi_1/ds');$$

and these equations are similarly interpretable, it being noted that $d\psi_1/ds'$ and $L'_{s'}$ are always positive. For very dilute solutions,

$$d\psi_1/ds' = 2R/(1-s')(2-\alpha+\alpha s').$$

If we may take $L'_{s'}$ constant between the concentrations 0 and s' , we obtain on integration

$$\Delta\tau \equiv \tau_0 - \tau = (f - \log c_1)R\tau_0/L'_0$$

for the lowering of the freezing-point due to the dissolved salt; for dilute and very dilute solutions we must take the values of $\log c_1$ as in III., and in the case of the latter, putting τ_0^2 for $\tau\tau_0$, we obtain van't Hoff's law,

$$\Delta\tau \doteq (1 - n_1/\Sigma n)R\tau_0^2/L'_0.$$

VI. If for any pressure p the lines $\psi_2 - \psi_b = 0$ and $\psi_1 - \psi_a = 0$, which are of the form $s = f(p, \tau)$ and $s' = F(p, \tau)$, are drawn on a $\tau\sigma$ -diagram, their intersection gives the *cryohydrate* point (i. e. Θ and Σ , the cryohydrate temperature and concentration) for that pressure; and it is shown that, if \mathfrak{U}_Σ and \mathfrak{L}_Σ are the total change of volume and heat of transformation per equivalent of the cryohydrate for solution in the cryohydrate solution,

$$d\Theta/dp = \Theta\mathfrak{U}_\Sigma/\mathfrak{L}_\Sigma, \quad d\Sigma/dp = (L_\Sigma U'_\Sigma - L'_\Sigma U_\Sigma)\Sigma/(\Theta\mathfrak{L}_\Sigma d\psi_1/d\Sigma),$$

the former being analogous to Clapeyron's formula.

VII. When the solution is in contact with the vapour of the solvent, there is condensation, equilibrium, or vaporisation according as

$$\psi_1 - \psi_v \begin{matrix} \geq \\ \equiv \\ \leq \end{matrix} 0,$$

ψ_v referring to the vapour. If s'' is the value of σ for equilibrium, and $U''_{s''}$ the volume-change and $L''_{s''}$ the latent heat of vaporisation, then

$$-\tau(\partial s''/\partial p)/U''_{s''} = \tau^2(\partial s''/\partial \tau)/L''_{s''} = 1/(d\psi_1/ds'');$$

hence, since $d\psi_1/ds''$ is always positive, the greater the concentration the lower the vapour-pressure and the higher the boiling-point.

Assuming as sufficiently approximate $U''_{s''} = v_2$ (the specific volume of the vapour), $L''_{s''} = \text{const.} = L_0''$, and $(p + \beta)v_2 = R\tau$ as the corrected Boyle's law (where $\beta = \text{const.}$), we obtain on integration

$$\Delta p \equiv p_0 - p = (p_0 + \beta)(1 - c_1 e^{-f}),$$

$$\Delta\tau \equiv \tau - \tau_0 = (f - \log c_1)R\tau\tau_0/L_0'',$$

for the lowering of the vapour-pressure and the elevation of the boiling-point respectively, which for very dilute solutions reduce to formulæ given by von Babo and Beckmann, viz.

$$\Delta p / (p_0 + \beta) = L_0'' \Delta \tau / R \tau_0^2 = 1 - n_1 / \Sigma n.$$

For less dilute solutions the value of $-\log c_1$ given in III. is to be taken; and with this and observations of $\Delta \tau$ the molecular state of the solute can be best determined.

In this investigation the solute has been taken to be not volatile.

VIII. Formulæ for the heats of dilution and solution are here given, which are somewhat complicated.

IX. Some relations between the foregoing magnitudes are discussed: notably we have

$$\pi / \Delta \tau = L_0' / \tau_0 v_1,$$

the osmotic pressure thus appearing to be independent of the concentration or degree of dissociation. If water is the solvent, we have generally $\pi / \Delta \tau = 916.18$, pressures being measured in cm. of mercury.

X. The measuring of concentrations in gm.-mol. *per litre* is reprobated, and the simplicity of the foregoing recommends our always taking $c_p \equiv n_p / \Sigma n$. R. E. B.

693. *Cryohydrates*. **M. Roloff**. (Zschr. phys. Chem. 17. pp. 325-356, 1895.)—Examples are given of the determination of the cryohydrate-point—*i. e.*, the intersection of the solubility and the freezing-point curves—for several mixtures of organic substances, such as benzoic-acid benzene and acetic-acid benzene. The author then proceeds to consider the effect of changes in external pressure on the cryohydrate-point, and experiments with a mixture of naphthalene and diphenylamine are described, which support his theory. S. S.

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